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April 1, 2011

Mr. Tien Q. Duong
EE-2G/Forrestal Building
Office of Vehicle Technologies
U.S. Department of Energy
1000 Independence Ave., S.W.
Washington D.C.   20585

Dear Tien,

Here is the first-quarter FY 2011 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from http://batt.lbl.gov/.

Sincerely,

Venkat Srinivasan
Manager
BATT Program

edited by: V. Battaglia
           M. Foure
           S. Lauer

cc: J. Barnes   DOE/OVT
       P. Davis   DOE/OVT
       D. Howell   DOE/OVT
       J. Krupa   DOE-BSO
       J. Muhlestein   DOE-BSO

FEATURED HIGHLIGHTS

Cell Analysis –

- **Chiang's Group produces a binder-free cathode with directionally aligned pores.**

- **Liu's Group demonstrates that pre-treating Si particles improves their reversible capacity.**

Anodes –

- **Dillon, George, and Lee's Group managed to create 15 μm thick films of amorphous Si with a capacity of 2500 mAh/g.**

Electrolytes –

- **Kerr's Group develops a single ion conducting polymer with low impedance.**

- **Smith and Borodin determined the pathway of PC in the presence of a salt and deterimed that the anion participates in the reaction, lowering the predicted oxidation potential.**

Modeling

- **Srinivasan's Group simulates hysteresis of charge/discharge behavior seen of materials with flat voltage profiles.**

Awards

- **Scott Mullin, Balsara Group, has won the 2011 Padden Award from the Division of Polymer Physics of the American Physical Society. The title of his presentation was:** Electric Field Induced Ordering of a Battery Electrolyte.
The award in honor of Frank J. Padden Jr., honors a graduate student for *"Excellence in Polymer Physics Research"*. This is a competition wherein students (international and domestic) are invited to submit their abstracts for the award. The Division picks 9 finalists and they give talks at a special symposium at the Annual March meeting of the Society which was last week. The committee selects the winner after the symposium.

BATT TASK 1
CELL ANALYSIS

TASK 1.1 - PI, INSTITUTION: Vincent Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis - Electrode Fabrication and Failure Analysis

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy systems: low energy; poor cycle life; poor calendar life

OBJECTIVES: 1) Provide electrodes, cells, and/or cycled cell components to BATT researchers. Bring fundamental understanding to electrode construction. Provide a comprehensive, independent assessment of promising materials designed to meet high-energy performance and cycling requirements, and allow for the differentiation between material failures and electrode/cell failures. 2) Determine some of the source/s and/or cause/s of cell failure.

GENERAL APPROACH: Objective 1) accomplished through methodically changing different aspects of the electrode fabrication process and examining the result of the changes *via* electrochemical and physical and chemical characterization techniques. Objective 2) accomplished, primarily, through electrochemical characterization of electrodes against different counter electrodes and then performing *ex situ* physical characterization studies, such as EDX, ICP, SEM, and TEM.

STATUS OCT. 1, 2010: There appears to be a correlation between Young's modulus and cycle life for cells with PVdF - the smaller the Young's modulus the longer the life. Full cells self discharge; VC modifies the self discharge of a full cell but does not affect the self discharge of graphite in half cells. The oxidation of the electrolyte has three regimes: <4.3 V; 4.3 V< > 4.6 V; > 4.6V. Binder systems containing SBR result in less 1st cycle irreversible capacity loss but do poorly at protecting the anode during long-term cycling.

EXPECTED STATUS SEP. 30, 2011: Good electrodes of $LiNi_{1/2}Mn_{3/2}O_4$ will have been distributed to BATT PIs. The solubility of different Mn compounds will have been measured. The rate of side reaction on both electrodes in a Graphite/NCM cell will be known. The dissolution of a high-voltage cathode will be known.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l; 5000 deep-discharge cycles; 15 years.

MILESTONES:
(a) Procure 20 g of a good source of $LiNi_{1/2}Mn_{3/2}O_4$. (Jan. 11) **Complete**
(b) Supply laminates of $LiNi_{1/2}Mn_{3/2}O_4$ that cycle 100 cycles. (Apr. 11) **On schedule**
(c) Report the solubility of Mn compounds. (Apr. 11) **On schedule**
(d) Report the rate of side reaction of NCM *vs*. Li and *vs*. Graphite. (Jul. 11) **Complete**
(e) Report the rate of side reaction of $LiNi_{1/2}Mn_{3/2}O_4$ *vs*. Li. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

(a) Procure 20 g of a good source of LiNi$_{1/2}$Mn$_{3/2}$O$_4$. (Jan. 11) **Complete**.
300 g of a Ni-spinel was obtained from NEI Corp. through Yet-Ming Chiang of MIT. 300 g of a similar material was obtained from Nippon Denko. The electrode fabrication process of these materials is proceeding. Preliminary analysis showed that the two materials have quite different voltage curves. Ni-spinel is not new and many researchers have found that doping with different transition metals improves the performance. The exact composition of the materials obtained will be assessed with the use of EDX in the near future. A process developed by Gerd Ceder for making Ni-spinel is being duplicated and improved upon here at Berkeley. This material will have no doping and may serve as a baseline.

(b) Supply laminates of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ that cycle 100 cycles. (Apr. 11) **On schedule**.
As mentioned under the first milestone, capabilities are being perfected to make good electrodes of Ni-spinel powders.

(c) Report the solubility of Mn compounds. (Apr. 11) **On schedule**.
Efforts have started in this direction. Initially, fresh powders of Ni-spinel will be tested for dissolution.

(d) Report the rate of side reaction of NCM *vs*. Li and *vs*. Graphite. (Jul. 11) **Complete**.
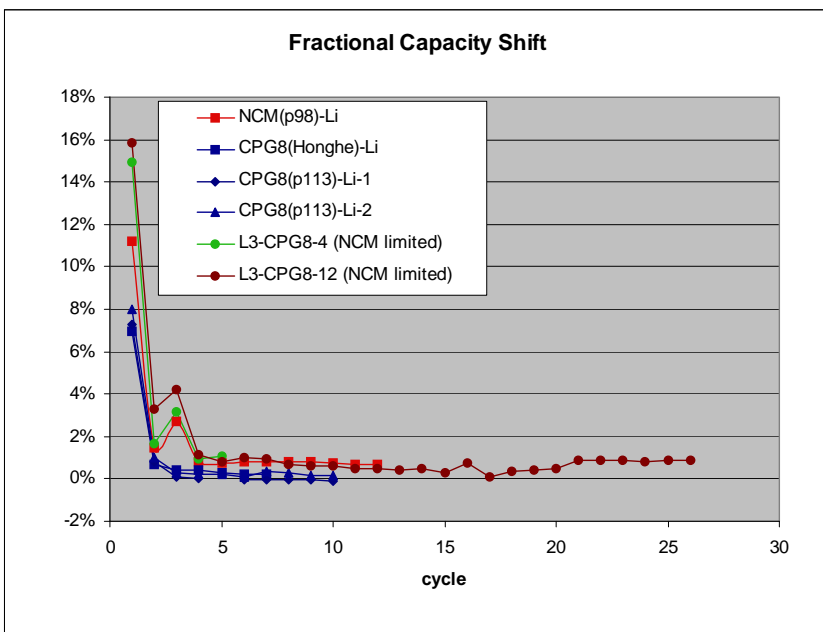
As mentioned in the last quarterly, a three electrode coin cell was fabricated. This cell allows us to follow the performance of the anode and cathode independently. The degree to which the electrode shifts with cycling for the cathode and anode was measured using this cell. In the absence of capacity fade, this is a direct measure of the amount of side reaction at each electrode. The figure shows the fractional shift of the capacity with cycling for cells of Li/NCM, Gr/NCM, and Li/Gr. The data shows that the level of capacity shift per cycle is the same for the Li/NCM and Gr/NCM cells, which is 3 times greater than the capacity shift of the Li/Gr. cells. Such a phenomenon could be attributed to an electrochemical shuttle.

(e) Report the rate of side reaction of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ *vs*. Li. (Sep. 11) **On schedule**.
The same techniques used in milestone (d) on NCM will be implemented on Ni-spinel. A method for making good electrodes must be developed first, as mentioned in milestone (b).

TASK 1.2 - PI, INSTITUTION: Thomas Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – High-energy Density Cathodes and Anodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000cycles/58 MWh).

OBJECTIVES: Synthesize and evaluate new electrode materials with improved energy density. Investigate the relationship of structure, morphology and performance of cathode and anode materials. Explore kinetic barriers, and utilize the knowledge gained to design and develop electrodes with improved energy density, rate performance and stability.

GENERAL APPROACH: Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports. Synthesize novel materials and/or unique structures and employ XRD, electron microscopy, vibrational spectroscopies, and electroanalytical techniques to determine their applicability to BATT goals. Characterize known and modified electrode materials and establish correlations between crystal structure, morphology and performance. Provide guidelines for materials synthesis and electrode fabrication processes.

STATUS OCT 1. 2010: We have shown that prelithiated silicon and tin powders have greatly reduced first-cycle capacity losses and exhibit superior cycling stability to elemental Si and Sn powders. Similar synthetic procedures can also be used to partially or fully prelithiate carbon anodes. The high reactivity of the prelithiated materials mandates use of non-oxidizing binders and solvents. Several alternative cathode materials containing cobalt and copper were prepared by ion exchange and by direct solid state synthesis. Their electrochemical properties were disappointing, however, and work on these materials has been concluded. A new technique for visualizing charge distribution in lithium battery electrodes has been developed in collaboration with staff at the Advanced Light Source and applied to cathodes in cross section and in the current collector plane.

EXPECTED STATUS SEP. 30, 2011: A new set of novel 4 V class cathode materials with capacities exceeding 200 mAh/g will have been synthesized and their potential utility evaluated. Appropriate binder/solvent combinations will have been identified for use with prelithiated intermetallic anodes. Charge distribution diagnostics will have been applied to electrodes harvested from commercial cells.

RELEVANT USABC GOALS: 40-mile PHEV: Energy/Weight 96 Wh/kg; CD Cycle Life 5000 cycles; Calendar Life @ 40°C 15 years.

MILESTONES:
(a) Report results of current and charge distribution assessments of harvested cathodes. (Feb. 11) **On schedule**
(b) Report on capacity retention in Si-based alloys with reduced irreversible capacity. (Mar. 11) **On schedule**
(c) Report capacities and charge-discharge potentials for new cathode materials. (Jun. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Cathodes: In collaboration with Marca Doeff, the ultrasonic spray pyrolysis method used to produce micron-sized, nanoporous spheres was applied successfully to the preparation of $LiCoPO_4/C$. This material, with two discharge plateaus of about equal capacity at 4.8 and 4.7 V and a theoretical capacity of 167 mAh/g, has suffered from poor utilization, rate performance, and cycling stability. Nanoporous microspheres (Fig. 1) consisting of *ca.* 70 nm-sized, carbon-coated, $LiCoPO_4$ primary particles were prepared by spray pyrolysis from aqueous precursor solutions. The carbon content wt%.
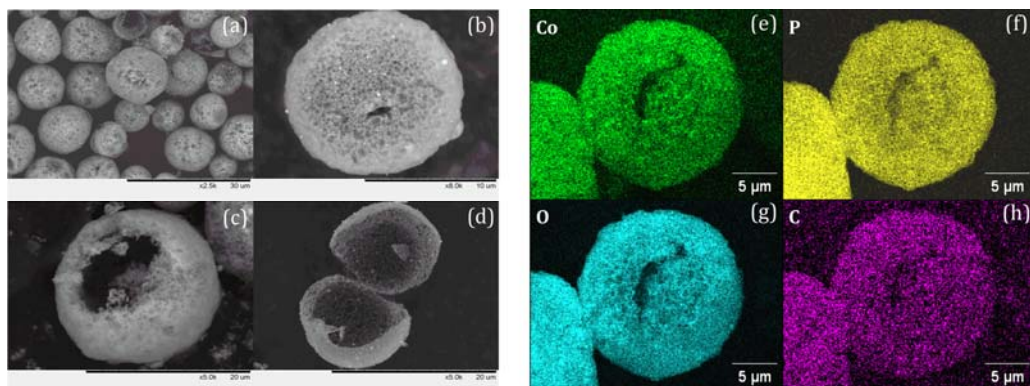

Figure 1. SEM images of (a) the nanoporous $LiCoPO_4/C$ particles; (b) the surface of a single particle; (c, d) broken particles, showing the 3D interconnected pores; EDS maps of (e) Co, (f) P, (g) O, and (h) C for a single particle.

Electrodes containing 10 wt% carbon black and 5 wt% PTFE exhibited excellent rate capability in Li half-cells, delivering 123 mAh/g at C/10 and 80 mAh/g at 5C. The capacity retention at C/10 was 95% after 20 cycles with coulombic efficiencies of 97% per cycle after the first cycle.
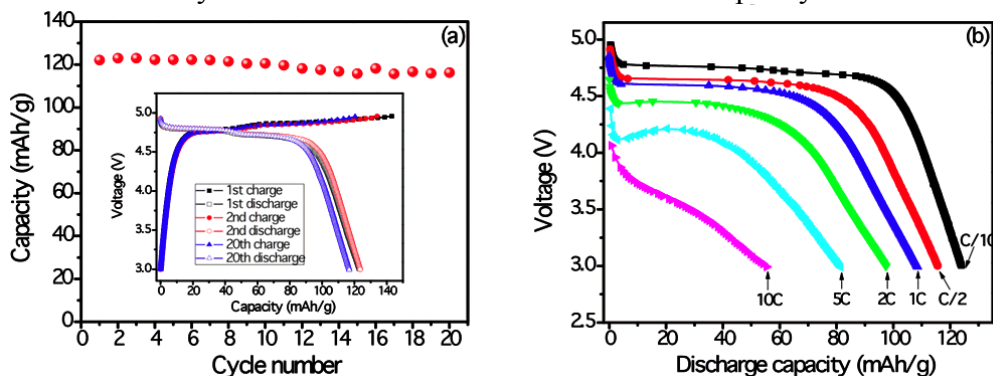

Figure 2. (a) Charge-discharge profiles at C/10, (inset) capacity retention and coulombic efficiency at C/10; (b) Discharge profiles at varying rates.

Anodes: Progress has been delayed due to the departure of Dr. C.-M. Park to a professorship at Kumoh National Institute of Technology, Gumi University, Korea.

Diagnostics: Progress has been delayed due to the departure of Dr. Jun Liu to DuPont R&D.

Collaborations: Groups of Guoying Chen, Robert Kostecki, Marca Doeff, Venkat Srinivasan, Jordi Cabana, and Karim Zaghib, as well as the staffs at NCEM, ALS, and SSRL.

TASK 1.3 - PI, INSTITUTION: Karim Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Analysis – Interfacial Processes: SEI Formation and Stability on Cycling

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy and poor cycle/calendar life

OBJECTIVES: Synthesis and evaluation of high voltage cathode (spinel Mn-Ni) with improved electrochemical stability. Reduce the oxidation of the cathode composition, electrolyte, and separator. Find the appropriate alternative anode material composition that meets the requirement for low cost and high energy. We will continue the development of binders for the cathode and alternative anode to understand and improve the properties of the SEI layer.

APPROACH: Our approach is to develop an appropriate method to stabilize the interface reaction of the high-voltage oxide (Mn-Ni based, *e.g.*, $LiMn_{1.5}Ni_{0.5}O_4$) cathode by surface coating with a more stable material such as an olivine. The emphasis is to improve electrochemical performance at high voltage. The effect of the type of binder, electrolyte composition, and separator on performance at high voltage will be investigated. Our research on high capacity anodes will focus on Si-based compositions that will be optimized by varying the graphite and SiO_x content.

STATUS OCT. 1, 2010: Due to the decision by the BATT Program, we redirected our project to investigate Si-based anode alloys, $LiMn_{1.5}Ni_{0.5}O_4$ cathode, and stability of the SEI. This effort started in August 2010 by exploring an appropriate composition of anode material based on carbon-coated nano-silicon, SiO_x and graphite. Work on the high-voltage cathode by reducing its oxidation reactivity with the electrolyte was addressed.

EXPECTED STATUS SEP. 30, 2011: Due to its low cost and high capacity, the development of silicon-oxide anodes will continue to achieve the DOE objectives, and research will be conducted to find a suitable composition of the Si-based high capacity anode. Different anode composition; pure Si and its mixture with SiOx and graphite will be investigated. For the cathode, high-voltage cathodes based on Mn-Ni spinel oxide will be used in this work. In order to reduce the oxidation of the electrolyte at high voltage, more stable binders, different electrolyte composition, carbon additives and surface coating of the cathode will be considered. In addition, investigation of the SEI layer on the anode and cathode, in particular the role of the binder type, electrolyte composition, and the cathode and anode composition will continue.

RELEVANT USABC GOALS: High energy and low cost: 96 Wh/kg (PHEV, 40 miles). Cycle life, calendar life: 15 year life (at 40°C).

MILESTONES:
(a) Optimize a silicon-based composition as anode material. (Feb. 11) **On schedule**
(b) Demonstrate the benefit of surface coating of high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ cathode with $LiFePO_4$ olivine material. (Sep. 11) **On schedule**
(c) Complete study of the effect of the binder type and electrolyte on the SEI layer by *ex situ* and *in situ* SEM analysis. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

During the last quarter, our post-mortem analysis showed that the bigger anode particles (*ca.* 13 μm) start to crack at around 0.1V. During the charging process, all of the cracks remained - some fissures collapsed and others swelled. In general, it appeared that the smaller particles (< 2μ) did not crack. These experiences should provide better understanding of the cycling mechanism of this anode and the failure mode associated with its capacity fade. The SiO anode material was evaluated using a binder of poly(acrylonitrile butadiene). The first cycle showed a reversible capacity of 1000 mAh/g and coulombic efficiency of 80%, and 98% in the second cycle. The cycle life was determined at a cycling rate of C/6 between 2.5 and 0.010 V. The capacity dropped from 800 mAh/g to less than 400 mAh/g after the first 60 cycles. When a 1-hour float step was added between cycles, the capacity remained stable at 800 mAh/g (Fig.1).
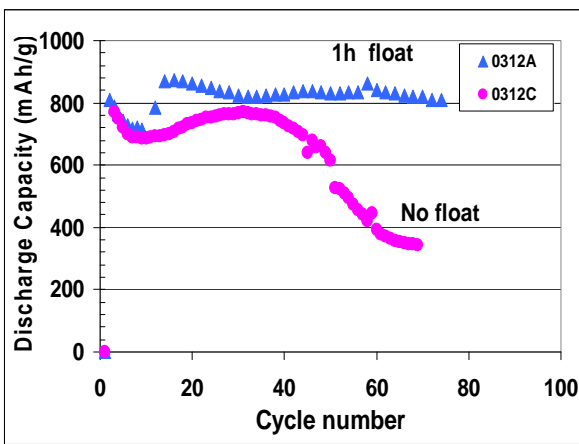

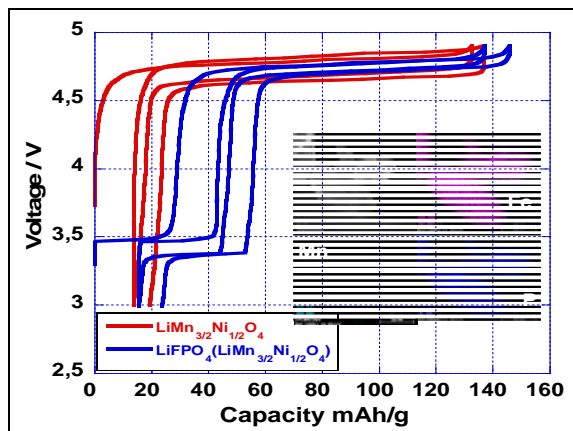**Figure 1.** Cycling of Li/Ec-DEC-1MLiPF$_6$/SiOx:Gr (1:1) cell at C/6.

Figure 2. First few cycles of Li/EC-DEC 1MLiPF$_6$/LiFePO$_4$(LiMn$_{1.5}$Ni$_{0.5}$O$_4$). Inset: elemental mapping of LFP-coated spinel LiMn$_{1.5}$Ni$_{0.5}$O$_4$.

In this quarter, an investigation of the high-voltage-spinel cathode material (LiMn$_{1.5}$Ni$_{0.5}$O$_4$) was initiated, as recommended by BATT. A major part of our task is to protect the surface of this cathode by a stable material to limit the side reactions. One of the materials chosen as a surface coating was LiFePO$_4$. To coat the spinel cathode with C-LiFePO$_4$, a dry process was used. In Fig. 2 (inset), HRTEM images with EDX confirmed the complete coating of the spinel particles, *i.e.,* no Mn or Ni was found on the surface.

The electrochemical evaluation of an uncoated material in standard electrolyte (EC-DEC-1M LiPF$_6$) cycled at C/24 between 4.9 and 3 V showed an EC1 (coulombic efficiency of cycle 1) of 91% with a reversible capacity of 108 mAh/g. The material coated with LiFePO$_4$ showed an EC1 of 85% and a reversible capacity of 123 mAh/g (Fig. 2). The cycle life of both cathode materials is under investigation.

HQ is continuing its collaboration with members in the BATT program: Vince Battaglia (LiFePO$_4$, graphite, and LTO) and John Goodenough (discussion on the new oxide and olivine material).

TASK 1.4 - PI, INSTITUTION: Yet-Ming Chiang, Massachusetts Institute of Technology

TASK TITLE – PROJECT: Cell Analysis – New Electrode Design for Ultrahigh Energy Density

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy system: low energy, poor cycle life

OBJECTIVES: Develop a scalable high density binder-free low-tortuosity electrode design and fabrication process to enable increased cell-level energy density compared to conventional Li-ion technology for a range of electrode-active materials.

GENERAL APPROACH: Develop fabrication methods for high density sintered cathodes and anodes with controlled pore volume fraction and pore topology. Electrochemically test electrodes in laboratory half-cells and small lithium ion cells (<100 mAh), and model electrode response. Aim to increase cell-level specific energy and energy density by maximizing electrode density and thickness, under operating conditions commensurate with USABC targets for PHEV and EV.

STATUS OCT. 1, 2010: First fabrication and test results from directionally freeze-cast and sintered $LiCoO_2$ electrodes were reported.

EXPECTED STATUS SEP. 30, 2011: 1) Fabrication and testing of at least two cathode materials in the proposed high density electrode approach; 2) Complete 2-3 experimental cycles of electrode fabrication by the directional freeze-casting approach, sintering, and electrochemical testing to establish capacity *vs.* C-rate behavior for at least one of the targeted cathode compounds.

RELEVANT USABC GOALS: EV: 200 Wh/kg; 1000 cycles (80% DoD).

MILESTONES:
(a) Report fabrication procedure, structural characterization, and initial electrochemical test data for directional freeze-cast and sintered $LiCoO_2$ electrodes in laboratory scale lithium half-cells. (Mar. 11) **On schedule**
(b) Report results of sintering process development study for high-density additive-free $LiNi_{0.5}Mn_{1.5}O_4$ electrodes. (Jun. 11) **On schedule**
(c) Report electrochemical test data for high-density additive-free $LiNi_{0.5}Mn_{1.5}O_4$ cathodes in laboratory scale lithium half-cells. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborator: Antoni P. Tomsia (LBNL)

Accomplishments: Building on the freeze-casting results of Q4 2010, experiments were focused towards increasing the degree of pore alignment and controlling/reducing the lateral pore spacing while increasing the overall sintered density. Previous work in the Tomsia lab on other materials has shown that freezing rate can influence the scale of the microstructures produced. In addition, hygroscopic additives such as sugar, glycerol, ethanol, methanol, and sodium chloride can alter the microstructure by changing the morphology of the freezing ice crystals. This approach was applied to $LiCoO_2$. Sintering of the freeze-cast preforms was conducted under different compositions and sintering conditions resulting in overall densities of 50 to 65%. Figures 1 and 2 show cross-sections taken parallel and perpendicular to the solidification direction for additive-free samples solidified from 30 vol% $LiCoO_2$ suspensions at rates of (A) 5°C/min and (B) 1°C/min. These are compared with samples containing (C) 5 wt% ethanol and (D) 5 wt% sugar, solidified at 1°C/min. The largest impact on pore alignment and spacing occurs when the freeze-casting rate is decreased from 5 to 1°C/min, with the latter producing a highly-oriented porosity of *ca*. 20 µm scale with relatively few dendrite cross-arms. The ethanol and sugar additives increase and decrease, respectively, the pore size slightly at the same freeze-casting rate, and also produce a highly-oriented porosity. Sample (A) is similar to samples fabricated and electrochemically tested during the previous quarter, while samples (B) to (D) are clearly a step in the desired microstructural direction. Electrochemical testing of these samples has begun, with initial results showing high utilization (*ca*. 140 mAh/g) at C/10, as expected.
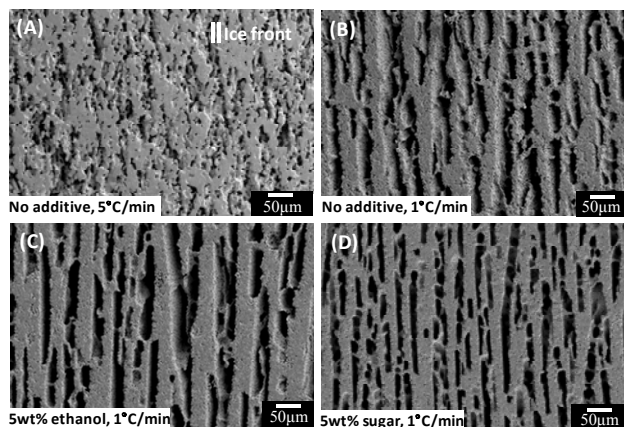

Figure 1. Cross-sections of directionally freeze-cast and sintered $LiCoO_2$ electrodes viewed parallel to the solidifying ice front. The upper panels show additive-free samples freeze-dried at 5 (A) and 1°C/min (B), in which the slower freezing rate is seen to produce greater uniaxial alignment of porosity. The lower panels show the effects of 5 wt% ethanol (C) and sugar (D) additive, which respectively produce coarser and finer aligned microstructures.
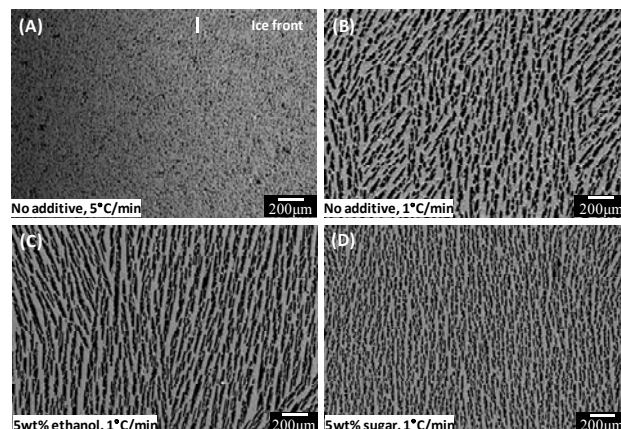

Figure 2. Cross-sections taken perpendicular to the freezing direction of the samples in Fig. 1.

TASK 1.5 - PI, INSTITUTION: Gao Liu, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – Advanced Binder for Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High energy system: poor cycle life, high first cycle irreversible capacity, low coulomb efficiency.

OBJECTIVES: Develop new conductive polymer binder materials to enable large volume change lithium storage materials to be used in lithium-ion electrode.

GENERAL APPROACH: Use functional polymer design and synthesis to develop new conductive polymers with proper electronic properties, strong adhesion and improved flexibility to provide electric pathways in the electrode, and to accommodate large volume/phase change of the active material during lithium insertion and removal.

STATUS OCT. 1, 2010: Gained fundamental understanding of the functions of the conductive polymer in the Si electrodes; assessed the pros and cons of the different methods to compensate for first cycle loss of the Si/conductive polymer electrodes; and demonstrate full cell cycling capability of the Si/conductive polymer negative electrode.

EXPECTED STATUS SEP. 30, 2011: Investigate conductive binder properties to Si electrode performance in various electrode compositions and configurations; explore binder functionalities to increase coulomb efficiency; and explore the conductive binders in other high capacity material systems.

RELEVANT USABC GOALS: PHEV-40: 144 Wh/l, 4000 deep-discharge cycles.

MILESTONES:
(a) Study conductive binder properties to Si electrode performance in various electrode compositions and configurations, aim to achieve 3.5 mAh/cm^2 loading electrode. (Mar. 11) **On schedule**
(b) Introduce binder functionalities to stabilized Si surface, minimize side reactions, and increase coulomb efficiency, aim to increase cycling efficiency from current 99 to 99.5%. (Sep. 11) **On schedule**
(c) Investigate the effectiveness of the conductive binders in other high capacity material systems. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

The surface properties of Si nanoparticles are an important aspect of Si electrode performance. The Si particle surface is obviously the interface between multiple phases of Si, binder, conductive additives, and electrolyte. The surface of the Si nanoparticles and its impact on the initial cell performance was investigated. Nanomaterials, including spherical particles, wires, or sponge structures, have enhanced surface area compared to micron-sized particles, therefore, surface impurities can play a significant role in the performance of the nano-material. The initial performance of Si nanoparticles with similar size distribution can vary significantly from batch to batch, even if they are from the same supplier, if the level of surface impurities is different. In this quarter, it was demonstrated that the performance variation of Si was attributable to the differences in the level of native oxide on the Si nanoparticles and that the removal of this layer using hydrofluoric acid (HF) significantly improved the Si nanoparticles' initial performance.
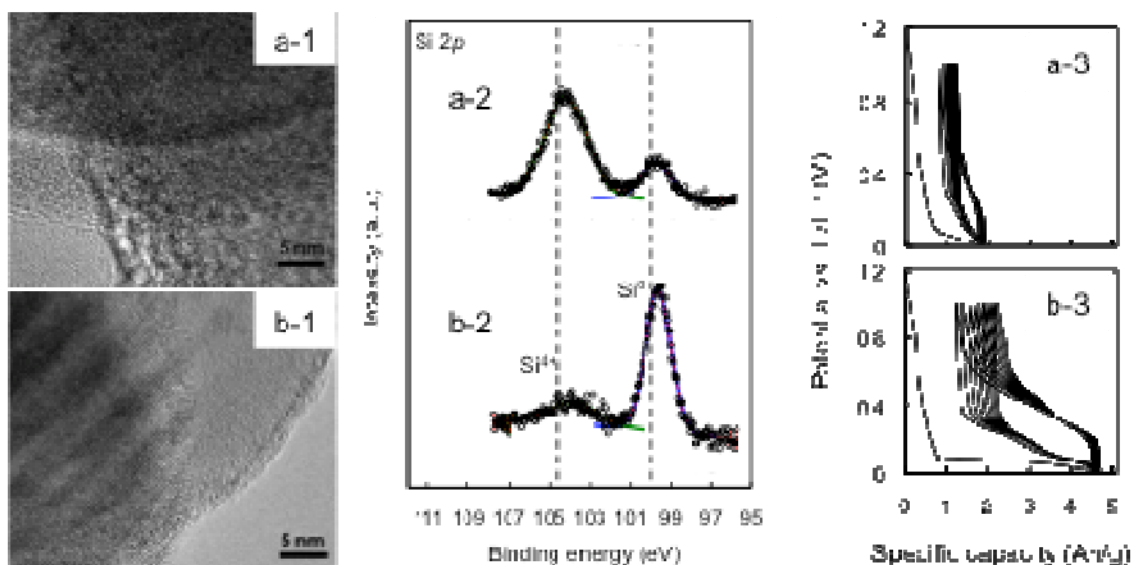

Figure 1. TEM images of a commercial, as-received Si nanoparticle (a-1) and after 30 min. of HF etching (b-1); Si 2p XPS spectra of Si particles for as-received (a-2) and after 30 min. of etching (b-2); specific capacity vs. potential of the first 10 cycles of Si electrode based on as-received Si (a-3) and after 30 min. of etching (b-3).

Based on this study, it can be said that the surface oxide layer on Si nanoparticles adversely affects the initial performance of an electrode by reducing the reversible capacity. Since thicker oxide layers result in lower reversible capacity, the surface oxide needs to be reduced to achieve better initial cycling performance. HF etching of commercial Si nanoparticles allows them to reach the theoretical specific capacity for the first few cycles. This study provides a clear interpretation of the origins of the performance variability of Si nanoparticles on the market and a general strategy to modify the surface chemistry and morphology of Si materials to improve the interface and, thus, enhance performance of high-energy Li-ion batteries.

Collaborations: Vince Battaglia, Venkat Srinivasan, Zhi Liu (ALS), Jordi Cabana.

TASK 1.6 - PI, INSTITUTION: Guoying Chen, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Analysis – High-Energy Cathodes: Improving Performance, Safety, and Cycle Life through Crystal Structure and Particle Morphology Design

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Available energy (Goal: 11.6 kWh); Cycle life (Goal: 5,000cycles/58 MWh).

OBJECTIVES: Explore phase-transition mechanisms and kinetic barriers of high-voltage and high-capacity cathode materials. Establish direct correlations between crystal structure, composition, morphology, performance and stability. Provide guidelines to design and fabricate cathode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

GENERAL APPROACH: Prepare well-formed crystals with various structure, composition, size and morphology using wet synthesis routes, such as solvothermal and molten-salt methods. Characterize their physical properties and investigate their solid-state chemistry using advanced spectroscopic, spectromicroscopic, scanning calorimetry, and electron microscopic techniques.

STATUS OCT. 1, 2010: Magnesium substitution in $LiMnPO_4$ was found to improve kinetics, structural, and thermal stabilities of the phosphate. Micron-sized $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC333) crystals with stoichiometric and excess amounts of Li were prepared by a molten-salt method. While the overlithiated oxide was well ordered with $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ super cells, the "Li-stoichiometric" sample lacks the same in-plane ordering in the structure. Chemical delithiation dissipates the cation ordering and disintegrates the overlithiated crystals, even at relatively low oxidation states with negligible volume change. Transformation from O3 to P3 structure occurred in both samples, but at a much higher oxidation state in the overlithiated sample.

EXPECTED STATUS SEPT. 30, 2011: Mixed transition-metal-phosphate crystals will have been prepared and evaluated for their kinetic performance and thermal stability. Layered oxide crystals with various Li, Ni, Co and Mn ratios will have been prepared. Structure analysis and property evaluation will have been performed on these crystals. Micron-sized Ni-Mn spinel crystals will have been synthesized.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles (80% DoD)

MILESTONES:
(a) Report the synthesis of layered oxide crystals with various compositions. (Mar. 11) **On schedule.** The modified $LiMnPO_4$ has been abandoned.
(b) Report the phase transformation and thermal behavior of $LiMMnPO_4$ (M = Mg, Fe, Co and Ni). (Jun. 11) **On schedule**
(c) Report structure and property evaluation of the layered oxide crystals. (Aug. 11) **On schedule**
(d) Report the synthesis of $LiNi_{0.5-x}Mn_{1.5+x}O_4$ crystals. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Layered Oxides: The impact of initial Li content on the structure and performance of layered oxides was investigated on micron-sized $Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2$ single-crystal plates ($x=0$ and 0.14). The excess Li in $Li_{1.14}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{0.86}O_2$ (alternatively $0.33Li_2MnO_3 \cdot 0.67LiNi_{0.5}Co_{0.5}O_2$) was found to increase the average oxidation state of the transition-metal ions, facilitate the formation of an in-plane $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ superstructure that converts R-3m to P3$_1$12 space group, improve the O3 phase stability, and decrease the unit cell volume change upon chemical delithiation. Figure 1a compares the charge and discharge profiles of the crystal electrodes during the first two cycles. At C/20 rate, an irreversible voltage plateau associated with O_2 release was observed at 4.4 V on the overlithiated oxide. The cathode delivered a discharge capacity of 175 mAh/g, as compared to 140 mAh/g by the stoichiometric material. On the dQ/dV plot (Fig. 1b), a second discharge peak at 3.3 V was observed, and the low-voltage charging peak shifted from 3.9 to 3.6 V after charging through the activation plateau. When cycled between 2.5 and 4.8 V, the overlithiated oxide showed improved capacity retention and rate capability (Fig. 1c), largely due to the enhanced phase stability during deep Li extraction at high voltages.
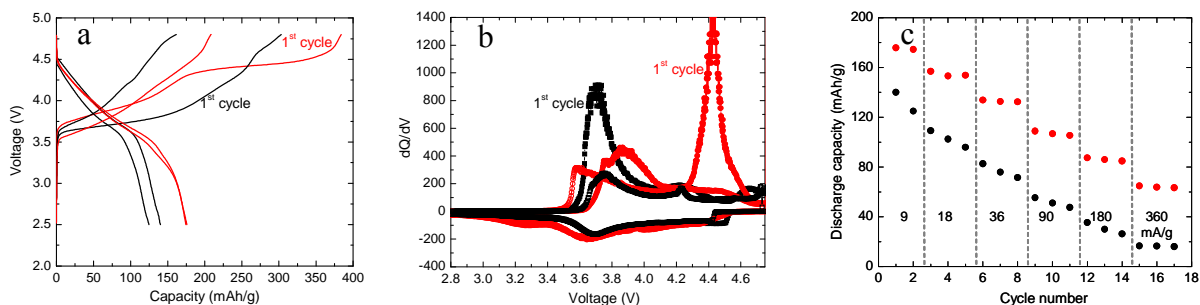

Figure 1. a) Charge-discharge profiles, b) dQ/dV plots for the first two cycles. Filled symbols: first cycle; open symbols: second cycle, and c) rate comparison of the oxides at the indicated current densities. Data for $x=0$ and 0.14 are shown in black and red, respectively.

Discrete $Li_{1.2}(Ni_{0.167}Mn_{0.667}Co_{0.167})_{0.8}O_2$ (or $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$) single crystals were also prepared by a molten-salt method. When nitrates were used as precursors, diamond-shaped crystals with an average size of 200 nm were obtained (Figs. 2a and 2b). Similar superlattice peaks between 20 and 30 degrees were observed on the XRD pattern (Fig. 2c), but the peak intensities were significantly higher compared to those of $Li_{1.14}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{0.86}O_2$, indicating improved ordering in $Li_{1.2}(Ni_{0.167}Mn_{0.667}Co_{0.167})_{0.8}O_2$. Property and performance evaluation of this Li- and Mn-rich oxide will be discussed in the next quarterly report.

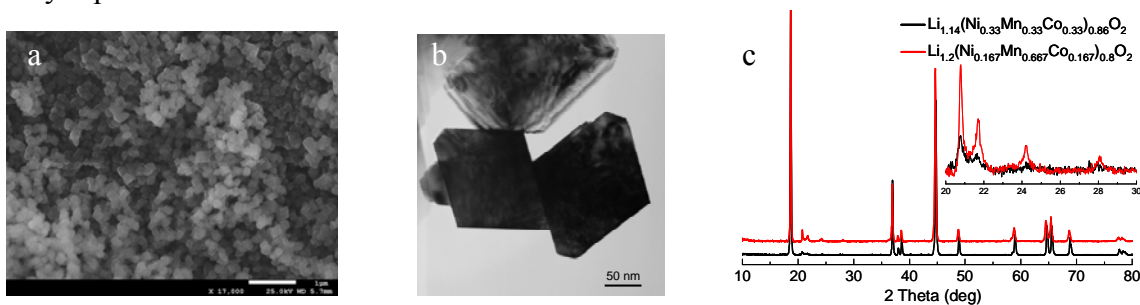**Figure 2.** a) SEM and b) TEM images of $Li_{1.2}(Ni_{0.167}Mn_{0.667}Co_{0.167})_{0.8}O_2$ crystals, and c) XRD patterns of the oxides.

Collaborations this quarter: Richardson, Kostecki, Doeff, Cabana, ALS, SSRL, NCEM.

BATT TASK 2
ANODES

Task 2.1-PI, INSTITUTION: Jack Vaughey, Michael Thackeray, Argonne National Laboratory

TASK TITLE – PROJECT: Anodes – Novel Anode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, poor low-temperature operation, and abuse tolerance limitations

OBJECTIVES: To address and overcome the electrochemical capacity limitations (both gravimetric and volumetric) of conventional carbon anodes by designing electrode architectures containing main group metal, metalloid or intermetallic components that can tolerate the volumetric expansion of the materials and provide an acceptable cycle life.

GENERAL APPROACH: Our approach is to search for inexpensive anode materials that provide an electrochemical potential at least a few hundred mV above the potential of metallic Li. The focus will be predominantly on Sn- and Si-based systems. A major thrust will be to design new electrode architectures in which an electrochemically-active species is attached to the surface of a porous current collector (formed by electrodeposition) providing a strong connection from the active species to the substrate. Additionally, electrodeposition processes will be modified to enable the use of various electrochemically active species and substrates. This is a new initiative for FY 2011.

STATUS OCT 1, 2010: In previous BATT efforts, significant progress was made in quantifying the energy and power advantages of three-dimensional electrode architectures over two-dimensional designs. Specifically, increased reversible capacity of Cu_6Sn_5 by electrodepositing Cu and Sn onto a Cu-foam electrode (also fabricated by electrodeposition) and manipulating the process to control the amount of free Sn in a composite Cu_6Sn_5-Sn electrode were reported.

EXPECTED STATUS SEP. 30, 2011: Three-dimensional architectures incorporating Sn and Cu, as well as other electrochemically-active elements and substrate materials, will have been designed. Processing parameters that control substrate porosity and conductivity will have been determined. Collaboration with industrially-interested partners will have been established.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Prepare metal anode architectures by electrodeposition and determine their electrochemical properties in lithium half cells and full cells. (Sep. 11)
(b) Determine processing parameters that control substrate porosity and electrical conductivity within metal foams. (Sep. 11)
(c) Initiate studies into processes involved in electrodepositing materials into confined spaces. (Sep. 11)
(d) Establish contact with industry, and undertake comparative studies of commercial Cu foams. (Sep. 11)

PROGRESS TOWARD MILESTONES

This project represents a new effort in the DOE OVT BATT Program initiated at the end of 2010. A focus of the project is to develop three-dimensional architectures for the anode electrode structure that will serve the joint purpose of helping to constrain the volume expansion that limits the cycle life of most main-group metal anodes while helping to increase the power by better integrating the current collector and the active material.

Building on our previous BATT project that studied the relationship between the electrode morphology and performance for a series of intermetallic (or alloy) electrode materials, an investigation was initiated into different ways to construct metal nets that can act to better bind the active material to the current collector.

The initial focus of this work was to develop a method to encase micron-size Si particles with a Cu net or mesh formed *in situ*. The use of micron-size Si particles (10 to 20 μm) allows for lower surface area contact with the electrolyte, thus eliminating losses due to SEI formation and allowing for easier handling of the raw materials. Initial attention was centered on optimizing the Cu coating on the Si particles. Using electroless deposition methods combined with a detailed annealing study, a set of conditions was identified where the deposited Cu coating annealed to form a three-dimensional network over the Si, binding it to the underlying Cu foil. Preliminary XRD studies showed that below $700^{\circ}C$ there was only a minimal amount of reaction between Cu and the Si particles to form the intermetallic phase, Cu_3Si, in agreement with the reported phase diagram. Using this method, a mesh was created over the Si *in situ*, binding it to the current collector without the need for additional binders or conductive additives.
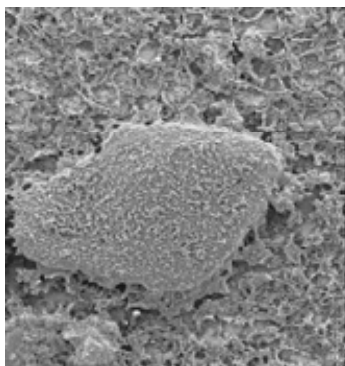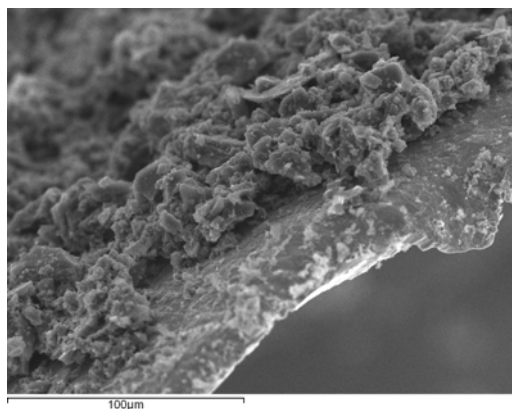
| (a) | (b) |

Figure 1. (a) shows a SEM image of the copper-coated silicon particle (20-25 μm) after annealing, (b) demonstrates how silicon is bound to the copper foil (edge-on view) after annealing.

Early electrochemical studies indicated an enhancement in power capability compared to more standard PVDF-based electrodes and a volume-expansion dependant cycle life. Work continues toward the optimization of the cycle life of these electrodes.

TASK 2.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes – Anodes: Novel Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, safety, and volumetric capacity limitations of Li-ion batteries

OBJECTIVE: To replace the presently used carbon anodes with safer materials that will be compatible with low -cost layered oxide and phosphate cathodes and the associated electrolyte.

GENERAL APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. Emphasis will be placed on simple metal alloys/composites from bulk to nano-size. An understanding of the tin-cobalt anode, the only commercial anode besides carbon, will help us discover why amorphous nanomaterials work. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal, kinetic, and structural stability to gain an understanding of their behavior.

STATUS OCT 1. 2010: It has been shown that bulk crystalline metals have a high capacity and react readily with Li, but their capacity faded rapidly after several deep cycles in carbonate-based electrolytes; and their behavior was no better under shallow cycling. In contrast, it has been shown that amorphous nano-size Sn alloys, unlike pure Sn, have a high capacity and maintain it on deep or shallow cycling, when stabilized with elements like Co. It also has been shown that nano-size manganese oxides, unlike crystalline vanadium and manganese oxides, are possible anode candidates when SEI formers, such as LiBOB, are added to the electrolyte. It was shown that small amounts of Si enhance the cyclability of Al.

EXPECTED STATUS SEP. 30, 2011: Our proposed work will result in the development of durable metal-based Li-ion battery anodes with volumetric energy densities that approach double those of the state-of-the art carbons. Nano-tin materials will be synthesized by at least two different approaches and then characterized, determining their morphology and electrochemical behavior. Some clues will be found as to how to control the SEI on such materials to optimize lifetime.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit, and maximum system volume.

MILESTONES:
(a) Synthesize nano-size tin materials by at least two different methods. (Mar. 11) **On schedule**
(b) Characterize these materials and determine their electrochemical behavior. (Sep. 11) **On schedule**
(c) Initiate studies on nano-silicon materials. Synthesize by at least one method. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

This quarter saw the conclusion of our investigation of novel anode materials. On January 1, 2011, a new anode project will be initiated, based on the competitively funded proposal of 2010. The milestones on the previous page reflect this new project. The accomplishments and conclusions of the completed project are summarized below.

Tin-Cobalt anodes. The structure and electrochemical behavior of amorphous nano-Sn-Co anodes was determined. The materials contained around 5 nm alloy particles embedded in carbon. They were found to cycle for many cycles without loss of capacity, unlike Sn foil where the capacity fell rapidly after only 10 to 12 deep cycles, or the equivalent of 10 to 12 full cycles when shallow-cycled at the 10% level. The rate capability was determined and found to be excellent for delithiation, *i.e.,* discharge of a full cell, but comparable to carbon for Li-insertion. A study of what reactions are actually occurring in the Co-Sn nano-particles is continuing under the DOE-EFRC-necces program. The latest results from the BATT Program were recently published: ref (1).

Aluminum-based anodes. The capacity of pure Al anodes fades rapidly on cycling in carbonate electrolytes; however, the eutectic Al-Si with 7.9 wt% Si showed much improved performance as demonstrated in our last report. The gravimetric capacity was 50% higher, around 700 mAh/g, than that of pure Al and doubled that of carbon. Volumetrically, it is far superior to carbon. One reason for the improved behavior with the Si doping is that all of the Li could be removed from the Al on charge. In contrast, after a few cycles there was always some LiAl present during cycling, even after completely charging. To better understand the possible reasons for this difference in behavior, careful structural studies of the starting materials were performed this quarter. It was discovered that around 2% Si was dissolved in the Al. This dissolution must be related to the nanosize of the Al, as micron-size Al and Si are totally insoluble at room temperature. In turn, it is possible that this dissolved Si changed the surface behavior of the Al so that an improved SEI layer was formed that did not close-off the LiAl from the electrolyte on charging. These results are now in press: ref (2).

Silicon. This work was covered in the last quarterly report - 4th quarter 2010.

The anode study is a collaboration with R. Kostecki (LBNL) and P. Chupas (ANL).

Further plans to meet or exceed milestones: None
Reason for changes from original milestones: No changes

Publications and Presentations:

(1) Ruigang Zhang and M. Stanley Whittingham "Electrochemical Behavior of the Amorphous Tin–Cobalt Anode," *Electrochem. Solid State Letters*, 2010, **13**: A184-A187.

(2) Wenchao Zhou, Shailesh Upreti and M. Stanley Whittingham "Electrochemical performance of Al-Si-Graphite composite as anode for lithium-ion batteries," *Electrochemistry Communications*, 2011, **13**: 158-161.

TASK 2.3 - PI, INSTITUTION: Prashant N. Kumta, University of Pittsburgh

TASK TITLE - PROJECT: Anodes – Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low specific energy and energy density, poor cycle life and coulombic efficiency, large irreversible loss, poor rate capability, and calendar life.

OBJECTIVES: To identify new alternative nanostructured anode materials to replace graphite that will provide higher gravimetric and volumetric energy density. The objective is to replace carbon with an inexpensive nanostructured composite exhibiting higher capacity (1200 mAh/g) than carbon while exhibiting similar irreversible loss (<15%), coulombic efficiency (>99.9%), and cyclability. The project addresses the need to improve the capacity, specific energy, energy density, rate capability, cycle life, coulombic efficiency, and irreversible loss limitations of silicon-based electrodes.

GENERAL APPROACH: Our approach is to search for inexpensive silicon, carbon, and other inactive matrix-based composite electrodes (powders rather than thin films) that provide 1) an electrochemical potential a few hundred mV above the potential of metallic Li, and 2) a capacity of at least 1200 mAh/g or greater (>2600 mAh/ml). Focus will be on exploring novel low-cost methods to generate nanoscale heterostructures of various silicon nanostructures and different carbon forms derived from graphitic carbon, nanotubes (CNT), and new binders. Other electrochemically inactive matrices will also be explored. Promising electrodes will be evaluated in half cells against metallic Li and compared to graphite as well as full cells. Electrode structure, microstructure, rate capability, long and short term cyclability, coulombic efficiency, as well as the origin and state of the SEI layers, will be explored.

STATUS OCT 1. 2010: Nano-scale electrodes comprising Si-graphitic carbon-polymer derived carbon and CNT-related systems have been successfully synthesized and analyzed in half cells. The nano-composite Li-Si-C structures exhibit stable capacities of 700-1000 mAh/g and higher.

EXPECTED STATUS SEP. 30, 2011: Efforts will continue to generate nano-composite 'core-shell', random, and aligned structures of varying nanoscale Si morphologies, boron (B), and C nanotubes exhibiting 1200 mAh/g and higher capacities. Research will be conducted to study the synthesis conditions, nano-scale microstructure affecting the energy density, rate capability, first cycle irreversible loss and coulombic efficiency, characterize the SEI layer, and outline steps to yield stable capacity, reduce irreversible loss, and increase coulombic efficiency.

RELEVANT USABC GOALS: Available energy for CD Mode, 10 kW Rate: 3.4 kWh(10 mile) and 11.6 kWh (40 mile); Available Energy for CS Mode: 0.5 kWh (10 mile) and 0.3 kWh (40 mile); 10s peak pulse discharge power: 45 kW (10 mile) and 38 kW (40 mile); Peak Regen Pulse Power (10 sec): 30 kW (10 mile) and 25 kW (40 mile); Cold cranking power at -30°C, 2sec-3 Pulses: 7kW; Calendar life: 15 years (at 40°C); CS HEV Cycle Life, 50 Wh Profile: 300,000 Cycles

MILESTONES:
(a) Achieve stable reversible capacity of 1200 mAh/g or higher. (Mar. 11) **On schedule**
(b) Irreversible loss (<15%) and efficiency (>99.9%) to match carbon. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

In the 2010 annual and quarterly reports, it was shown that Si/C based nano-composite anodes, successfully synthesized by either high-energy mechanical milling (HEMM) or two-step chemical vapor deposition (CVD) method, displayed a reversible capacity of *ca*. 1000 to 2000 mAh/g with excellent cyclability. However, the HEMM-derived materials exhibited greater than 25% 1st cycle irreversible capacity loss and/or low coulombic cycling efficiency, whereas the CVD-derived Si/C nano-composite anode showed a low irreversible loss (8 to 12%) and a low coulombic efficiency (*ca*. 98 to 99%). For the Si/C nano-composite anode to be commercially viable, the 1st cycle irreversible loss should be lower than 15% and have a coulombic efficiency in excess of 99.8%.
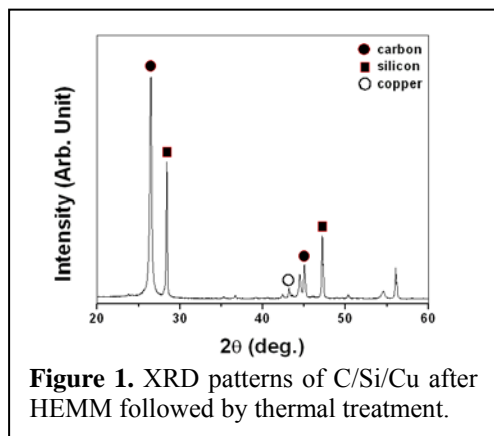
Accordingly, the effect of Cu on the 1st cycle

Figure 1. XRD patterns of C/Si/Cu after HEMM followed by thermal treatment.

irreversible loss and coulombic efficiency was studied. Figure 1 shows the XRD pattern of HEMM-derived C/Si/Cu nano-composite thermally treated at 1073 K for 6 h. The XRD pattern of the nanocomposite in Fig. 1 shows the presence of C, Si, and Cu and the absence of copper silicides or SiC. The cycling response of the C/Si/Cu nano-composite cycled for 30 cycles at *ca*. a C/5 rate (Fig. 2,) showed a 1st cycle discharge capacity of 940 mAh/g and a 1st cycle charge capacity of 769 mAh/g, which equates to an irreversible loss *ca*. 18%. The composite showed excellent capacity retention with a 0.30% loss per cycle for the first 30 cycles and an excellent coulombic efficiency of *ca*. 99.8%. The effect

Figure 2. Variation of specific capacity *vs*. cycle numbers of *nc*-Si/C composite cycled at C/7 rate.

of Cu to lower the irreversible loss and improve the coulombic efficiency will be studied and reported in the near future.

Long-term cycling of "binder-free" electrodes comprising 54 wt% nanocrystalline Si deposited onto vertically-aligned carbon nanotubes (CNTs) grown on Inconel was studied. The as-prepared electrodes exhibited a first-discharge capacity of 1870 mAh/g and a low irreversible loss of 16%. Cycling performance was studied at increasing current rates of 100 (C/15), 200 (C/7), and 400 mA/g (C/3.5). Figure 3 shows the cycling response. The material had a capacity retention of 1350 mAh/g after 30 cycles, 1000 mAh/g after 60 cycles, and 706 mAh/g after 90 cycles. The capacity fade was a

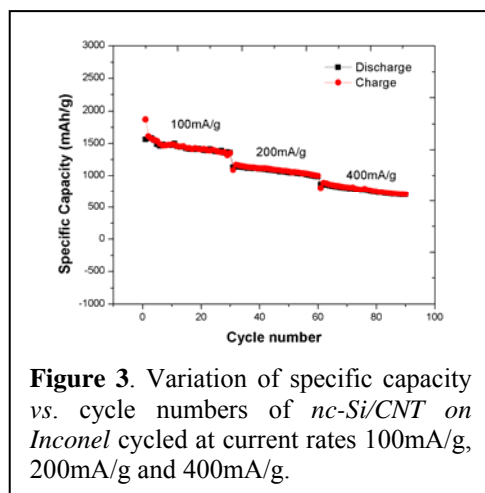**Figure 3**. Variation of specific capacity *vs*. cycle numbers of *nc-Si/CNT on Inconel* cycled at current rates 100mA/g, 200mA/g and 400mA/g.

reflection of the inadequacy of the CNTs-nanocrystalline / Si interface, which could be manipulated through engineering of the interface. These studies are currently on-going and will be reported subsequently.

TASK 2.4 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE – PROJECT: Anodes – Development of High Capacity Anode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, cost, poor cycle life and large irreversible capacity

OBJECTIVES: To develop high capacity, low cost anode with good rate capability to replace graphite in Li-ion batteries.

GENERAL APPROACH: Our approach is to manipulate the nano-structure and conductivity of Si and SiO_x to improve their mechanical and electrical stability. Both nano-sized and micro-sized Si particles with nano-pore structures will be investigated. The electronic conductivity of Si particles will be improved by CVD-coated carbon. Self-assembled templating method will be used to incorporate Si particles into graphene sheets to improve the electronic conductivity between Si particles and accommodate the volume variation of Si during cycling. The stability of SEI layers will be investigated by *in situ* TEM/SEM. New binders will be developed to improve the cyclability of a Si-based anode. Electrolyte and additives will be tailored to reduce the first cycle loss and stabilize SEI.

STATUS Oct. 1, 2010: Highly stable, free-standing SnO_2/graphene and TiO_2/graphene paper electrodes were successfully prepared with a unique self-assembly approach. These free-standing paper electrodes can operate with no extra current collector and conductive additive. Nano-TiO_2/Graphene composite demonstrated a capacity of ~170 mAh/g at 1C rate. SnO_2/graphene composite also demonstrated a capacity of ~790 mAh/g. Stable cycling and excellent rate capability were achieved in both composites. The electrochemical performances of nano Si and micro-sized Si particles with nano-pores was improved with a CVD-carbon coating. Self-assembled Si/graphene composites demonstrated a capacity of more than 1600 mAh/g Si for more than 35 cycles.

EXPECTED STATUS SEP. 30, 2011: The composition and cycling protocols of a Si/graphene hybrid electrode will be optimized to balance the high capacity and cycling stability. The initial irreversible capacity loss of a Si-based electrode will be minimized by adjusting the morphology/reactivity of the carbon matrix and developing new electrolyte/additives. Both conductive binders and pre-coated current collectors will be investigated to maintain a strong bonding among Si particles and between Si and current collectors during cycling.

RELEVANT USABC GOALS: > 96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:
(a) Identify optimized carbon matrix/additives with reduced first cycle loss. (Mar. 11) **On schedule**
(b) Improve coulombic efficiency through appropriate electrolyte/additives. (Sep. 11) **On schedule**
(c) Optimize new conductive polymers as a binder for Si anode. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

A novel method was developed to synthesize Si nanoparticles from Si-containing solid precursors. The nanosized precursors were used as the starting material; metal powders were used as the reducing agent. The electrode was made by a wet casting method after removing the reaction by-products. Figure 1 (a, b) shows the first charge/discharge profile and the cycle stability data of the *in situ* synthesized Si. A specific capacity of about 760 mAh/g based the whole weight of the electrode was achieved and it was very stable in the first 12 cycles. The capacity started to fade at a rate of 1.2% in the subsequent cycles.
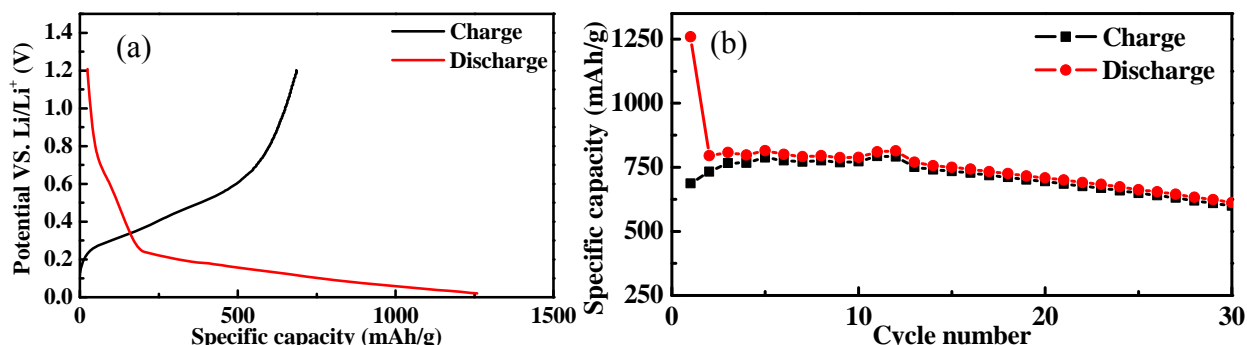

Figure 1. (a) First cycle charge and discharge profile. (b) Cycling stability at the current density of 160 mA/g.

Efforts were also made to synthesize Si nanoparticles using a solution phase method. Silicon nanoparticles were synthesized by the reduction of silicon chloride to produce a metal powder in a conductive framework of graphene and mesoporous carbon. After removal of the reaction side-products, the composite of silicon/graphene or silicon/mesoporous carbon was mixed with binder and cast into films. The initial capacity of the cell was relatively low, which was probably due to the residue of the by-products.

More work will be done to optimize the procedure used to synthesis Si nanoparticles from Si-containing precursors. In a separate effort, porous silicon with large pore sizes and more uniform structures will be investigated. These samples will be coated with a thin layer of carbon by CVD. Their capacity and long term cycling stability will be investigated.

Collaborations: I.A. Aksay, Princeton University, and Vorbeck Inc. have provided the graphene for this work. Prashant Kumta, University of Pittsburgh, assisted in depositing the Si nanoparticles on to novel carbon materials using CVD.

TASK 2.5 - PI, INSTITUTION: Anne Dillon, NREL; Steven George and Se-Hee Lee, University of Colorado, Boulder

TASK TITLE - PROJECT: Anodes – Atomic Layer Deposition for Stabilization of Amorphous Silicon Anodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Cost, low gravimetric and volumetric capacities, safety

OBJECTIVES: In this work we will utilize an inexpensive and scalable hot wire chemical vapor deposition (HWCVD) technique for the production of either amorphous silicon (a-Si) or nano-Si powders that are tailored for battery applications. We will also develop novel atomic layer deposition (ALD) coatings that will enable durable cycling to be achieved for the high volume expansion Si materials (~400 %)

GENERAL APPROACH: The a-Si or nano-Si powders will be fabricated with HWCVD *via* silane decomposition on a hot filament. Growth parameters will be explored to optimize yield and later incorporate dopants to produce more conductive a-Si as well as additives to improve cycling stability. Conventional electrodes containing active material, conductive additive and binder will be fabricated and subsequently coated via ALD that will serve as an artificial solid electrolyte interphase (SEI) and will importantly help minimize degradation upon volume expansion.

STATUS OCT. 1, 2010: This is a new award that will be initiated in FY11. However, following the BATT meeting at LBNL on July 27, 2010, Anne Dillon met with Yi Cui and Robert Huggins at Stanford to initiate a collaborative effort (July 28, 2010). We believe this will accelerate progress in both of these new Si awards. NREL and CU are also already undergoing staffing plans to prepare for the new project. NREL is also currently slightly modifying the HWCVD apparatus that was previously used for photovoltaic applications.

EXPECTED STATUS SEP. 30, 2011: A thick Si anode with an ALD coating will be demonstrated to have a high durable capacity. Both gravimetric and volumetric capacities will be optimized.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES
(a) Optimize HCVD produced a-Si or nano-Si in conventional coin cell. (Jan. 11) **Complete**
(b) Demonstrate scale-up of HWCVD a-Si or nano-Si powder. (May 11) **On schedule**
(c) Demonstrate an ALD coating for improved performance of Si anode. (Jul. 11) **On schedule**
(d) Optimize coated electrode and demonstrate durable cycling. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

(a) Demonstrate scale-up of HWCVD *a*-Si or nano-Si powder. (January 2011) **Complete**
Scale-up of hot-wire, chemical-vapor-deposition (HWCVD), phase-pure, amorphous silicon (a-Si) was achieved as delineated in detail below. Progress was also made towards the demonstration of our next two milestones as mentioned at the end of this report. Note that this is a joint award with the University of Colorado (CU). The money for CU was recently received and the sub-contract is proceeding.

This quarter the focus was on the deposition of *a*-Si powders that would be suitable for thick electrode fabrication with conventional additives. Amorphous Si has been demonstrated to exhibit improved cycling performance but has not achieved durability and rate capability for needed in PHEVs and EVs. In addition, *a*-Si has only been demonstrated for thin films, significantly <1 μm, and in nanostructured electrodes that were not suitable for large-scale vehicular applications. NREL has a long history of depositing thin films of HWCVD *a*-Si for solar cell applications. However, in scaling up the process for batteries, the synthesis conditions were found to be critical to achieving a phase-pure amorphous powder with high-density.

In all of our HWCVD depositions of *a*-Si powders, the substrate temperature (T_s) was at room temperature. It was believed that this would completely remove the possibility of growing any crystalline Si species (*c*-Si). However, we found that local hot spots, depending on proximity of the filament to the substrate and duration of the run/film thickness, could result in the nucleation of *c*-Si particles. Figure 1a) displays an *in situ* microscope image taken while acquiring micro-Raman spectroscopy measurements. The magnification is 100 times and the green spots represent the μ–Raman spot size. In these initial experiments the large particles observed in Fig. 1a) were *ca*. 30 μm in diameter and in general had a Raman line consistent with *c*-Si, blue curve in Fig 1b). Other portions of the initial samples appeared completely amorphous, red curve Fig. 1b), and a mixed phase was also observed, depicted by the orange curve in Fig. 1b).

By optimizing the synthesis conditions, pure amorphous powder was produced as shown in the micrograph of Fig. 1 c) and the Raman spectrum of Fig. 1 d). X-ray diffraction of the a-Si powders showed no crystalline peaks, and 15 μm electrodes containing 60:20:20 *a*-Si:AB:PVDF displayed a voltage profile consistent with that of *a*-Si. An initial capacity of *ca*. 2500 mAh/g (normalized to the entire electrode weight) was obtained. The electrodes were subsequently coated with our previously demonstrated Al_2O_3 ALD coating (≤1 nm thick) and the 1st cycle coulombic efficiency was improved from 60 to 80%. Hence, electrode and coating optimization are still required to achieve durable cycling and reduce the first cycle capacity loss.
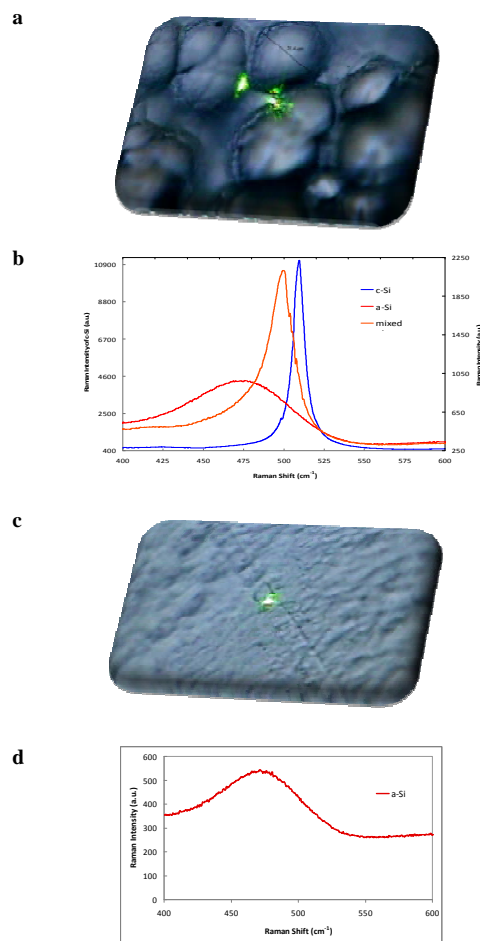
Figure 1: a) Topographical image of mixed phase HWCVD Si and **b)** corresponding Raman spectra compared with **c)** image of optimized *a*-Si and **d)** corresponding Raman spectrum.

TASK 3.1 - PI, INSTITUTION: Nitash Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – Development of Polymer Electrolytes for Advanced Lithium Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Improved energy density and safety.

OBJECTIVES: Characterize PS-PEO electrolytes with LiTFSI against Li-metal anodes in symmetric cells, sulfur, and air cathodes. Use block copolymers to create mesoporous battery separators for conventional liquid electrolytes.

GENERAL APPROACH: Synthesize and characterize dry PS-PEO (and PS-PEO-PS) polymer electrolytes. Continue to characterize salt/polymer mixtures by AC impedance spectroscopy, and make DC measurements with Li | polymer electrolyte | Li cells to obtain diffusion coefficients and Li transference numbers. Collaborate with members of the BATT Program to test stability of the electrolyte against electrodes (Li metal, sulfur, and air). Synthesize and characterize porous PS-PE polymer separators by synthesizing a block copolymer, blending with a homopolymer, and washing out the homopolymer to yield a porous block copolymer.

STATUS OCT. 1, 2010: Completed study of effect of morphology on diffusion coefficient and solubility of Li_2S_x in PS-PEO copolymers. Used membrane casting device to create first Li|polymer electrolyte|air cells. Identified ideal molecular weight of homopolymer for creating block copolymer-based separators. Initiated project on electronically- and ionically-conducting polymer binders.

EXPECTED STATUS SEP. 30, 2011: Complete study of effect of morphology on transference number and diffusion coefficients in PS-PEO copolymers. Obtain conductivity-morphology relationships in block copolymer-based separators with well-defined pores. Study polysulfide dissolution in Li|SEO|S cells. Study the effect of cathode composition and morphology on Li|SEO|air cells. Synthesize copolymers that conduct both electrons and ions.

RELEVANT USABC GOALS: EV applications goals are a specific energy of 200 Wh/kg and a specific pulse power of 400 W/kg.

MILESTONES:
(a) Measure transference number as a function of morphology of SEO. (Mar. 11) **On schedule**
(b) Complete synthesis of electronically- and ionically-conducting binder (Jun. 11) **On schedule**
(c) Report on cycling characteristics of Li|PS-PEO|air cells as a function of cathode composition and morphology. Go/no go decision based on improvement of one of the key limitations of current Li/air cells: capacity fade due to water contamination. (Sep. 11) **On schedule**
(d) Quantify the relationship between conductivity and morphology of porous block copolymer separators (Sep. 11). **On schedule**
(e) Quantify the effect of nanostructure on thermodynamics of SEO/polysulfide thermodynamics (Sep. 11). **On schedule**

PROGRESS TOWARD MILESTONES

Regarding milestone (a), a new cell was built to perform the concentration cell experiments needed to obtain accurate transference numbers from polymer electrolytes. The measurement of the dependence of transference number on morphology in SEO is on track.

For milestone (b), the polymer poly(3-hexylthiophene)-block-poly(ethylene oxide) (P3HT-*b*-PEO) was successfully synthesized using a combination of Grignard metathesis synthesis (GRIM) polymerization and click chemistry. Two molecular weight batches were prepared for analysis: a 6K-2K and a 5.2K-4.8K combination of P3HT and PEO. Battery cycling data focused on the 6K-2K sample, with the cathode material being comprised of P3HT-*b*-PEO, a small amount of LiTFSI (r=0.085), and 50% LiFePO$_4$ by weight. Specific capacities around the theoretical value for LiFePO$_4$ were observed, with coulombic efficiencies at 90% or higher.

For milestone (c), the charge and discharge voltages were determined to be strongly dependent on the cathode composition. It was found to be quite sensitive to cathode thickness and amount of compression, as both contributed significantly to the resistance of the cathode. In addition, the voltage of charge was especially sensitive to the type of catalyst used. There were preliminary indications that side reactions, such as electrolyte degradation, occurred above 4 V. Therefore, nanoparticle catalysts were concurrently being developed to enable charging below 4 V as well as examining the effect of morphology on this degradation.

The work toward milestone (d) is on schedule. A series of different molecular weight polystyrene homopolymers were blended with SES [poly(styrene)-block-poly(ethylene)-block-poly(styrene), 15k-79k-15k] to measure the effect of varying the α-value on conductivity. The α-value represents the ratio of the molecular weight of the homopolymer over the molecular weight of the styrene block in the SES. The conductivities as a function of α-value are plotted in Fig. 1 for two different void fractions. An optimal value of α around 0.35 was found. Separators prepared using both high (α>1) and low (α<0.2) α values displayed poor conductivity. The morphologies of these systems is currently being studied using nitrogen adsorption, SEM, and small angle X-ray scattering (SAXS).

Figure 1. Conductivity of SES (15k-79k-15k) with 1M LiPF$_6$ in EC/DEC as a function of α for two different void fractions.

Regarding milestone (e), the solubility of Li$_2$S$_x$ ($1 \leq x \leq 8$) compounds in SEO copolymer was concluded. In an attempt to quantify the relative concentration of each of the species present, ultraviolet-visible (UV-Vis) spectroscopy was performed on the polysulfide species in dimethylsulfoxide solution, poly(ethylene oxide) homopolymer, as well as SEO copolymer. Additionally, TEM images were taken of SEO(4.9 to 5.5)/Li$_2$S$_4$, r = 0.03 in an effort to corroborate some of the morphologies observed in the SAXS data.
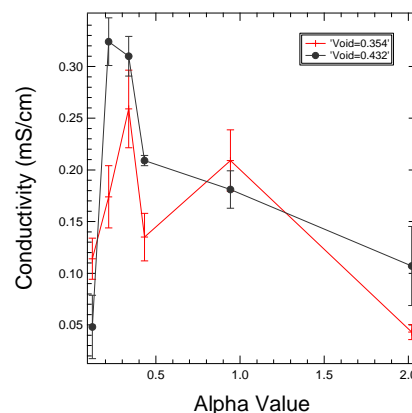
TASK 3.2 - PI, INSTITUTION: John Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes – R&D for Advanced Lithium Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor cycle and calendar life, low power and energy densities, particularly at low temperatures (-30^oC)

OBJECTIVES: 1) Determine the role of electrolyte structure upon bulk transport and intrinsic electro-chemical kinetics and how it contributes to cell impedance (Energy/ power density). 2) Determine chemical and electrochemical stability of electrolyte materials to allow elucidation of passivating layers (*e.g.*, SEI).

GENERAL APPROACH: A physical organic chemistry approach is taken to electrolyte design, where the molecular structure is varied to provide insight into the processes that may affect the performance of the battery. This involves model compounds as well as synthesis of new materials to test hypotheses which may explain battery behavior.

STATUS OCT 1. 2010: Reactivity of salt anions is a major contributor to interfacial impedance and the structure can be altered to reduce this**.** The behavior of single-ion conductor polyelectrolytes with cathodes was explored to confirm the benefits of such electrolyte systems with regard to electrode thicknesses and increased energy density. Silicon and tin alloy anodes were studied to evaluate the benefits of polyelectrolytes on large volume-change electrodes.

EXPECTED STATUS SEP. 30, 2011: Studies on composite electrodes using single-ion conductor binders will continue with the focus area materials: high voltage Ni-Mn spinel cathodes and Conoco Philips CPG-8 graphite anodes. The behavior of the single-ion binders will be compared with the base-line electrolytes. Detailed chemical analysis of the electrolyte degradation products will be completed. Work on high volume expanding anodes with single-ion conducting binders will be extended using Si–based alloys. Dry polymer systems will be tested with $LiFePO_4$.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10 s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile); *Cycle life*: 5000 cycles (10 mile) and 3000 cycles (40 mile); *Calendar life*: 15 years (at 40°C); cold cranking capability to -30^oC; abuse tolerance.

MILESTONES:
(a) Determine whether available single-ion conductor polyelectrolytes function with the high voltage NiMn spinel cathodes. (Apr. 11) **On schedule**
(b) Determine the stability of base-line and single-ion electrolyte to NiMn spinel cathodes, including chemical analysis of electrolyte degradation products. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

1) Use of single-ion-conductor(SIC) polyelectrolytes (gel and dry polymer) to provide high energy composite electrodes due to increased thickness. Single-ion-conducting polymers were prepared by reacting polysulfone and polyether polymers with various silyl groups that contained different anions. These are shown below as MDFB, F-MDFB and TFSI.

MDFB　　　　　　　　　　　　**F-MDFB**
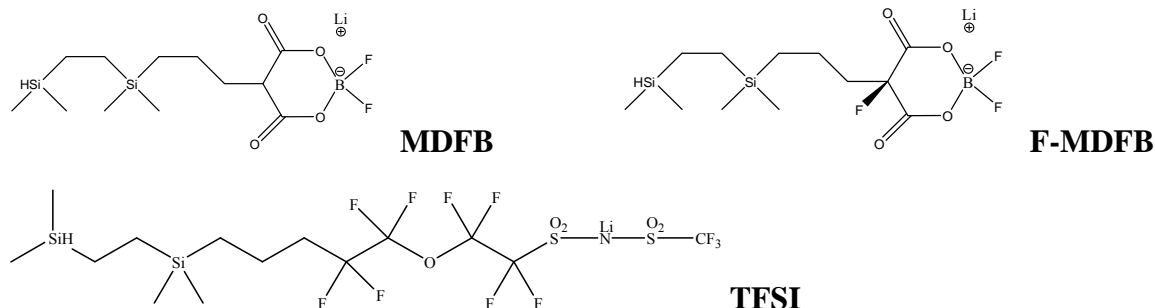
TFSI

The membranes were plasticized by addition of EC:EMC or *gamma*-butyrolactone solvents. The best performing SIC on Li metal was the polyether kinked with TFSI anion. The impedance behavior of this polyelectrolyte gel at different temperatures and cycling at 80°C at 0.1mA/cm^2 are shown below. The impedance behavior was greatly improved over previous SIC impedances (by two orders of magnitude) and the polarization on cycling was excellent.
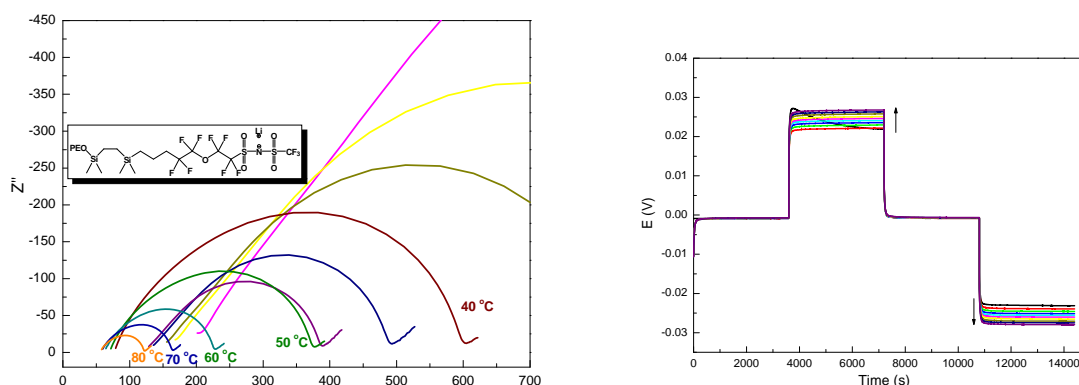
2) Modification of Carbon Nanotubes with lithium salts to reduce impedance. Carbon nanotubes were modified with sulfonated polystyrene and the acid groups were titrated with Li ions to give the Li salts. The modified carbon nanotubes were used as conductors in Li/LiFePO$_4$ cells with standard LiPF$_6$–EC:DMC electrolyte. The impedance behavior and high rate cycling of the electrodes with the modified nanotubes was excellent. This indicated that providing a high concentration of Li ions in the composite electrode was a viable approach to reducing the interfacial impedance. The impedance of the modified nanotubes was consistent with polyelectrolyte layers on electrodes.

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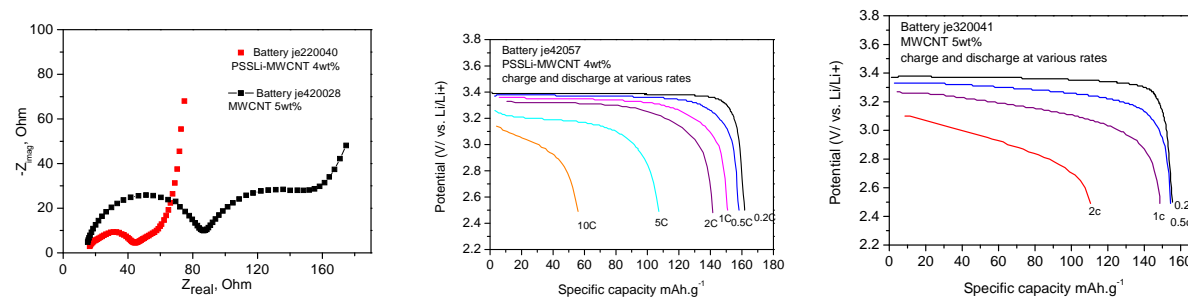
TASK 3.3 - PI, INSTITUTION: Grant Smith and Oleg Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes – Modeling: Molecular Modeling of Electrodes, SEI, Electrolytes, and Electrolyte/Electrode Interfaces

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor low temperature operation, transport through SEI layer and cycle life. High interfacial resistance. Low energy and power density.

OBJECTIVES: Prediction and investigation of structure and formation of the SEI at high energy density anodes using reactive MD simulations. Prediction and understanding of properties of novel high voltage electrolytes including oxidative stability and degradation products on the cathode. Prediction and understanding of charge transfer resistance to graphite and $LiFePO_4$ electrodes. Improved understanding of electric double layer structure, capacitance and transport as a function of electrode potential and temperature.

GENERAL APPROACH: Utilize developed force fields and simulation methods to simulate high voltage novel electrolytes. Utilize electroactive interface model to study electric double layer properties and charge transfer processes at the cathode/electrolyte and anode/electrolyte interfaces. Utilize reactive force field (ReaxFF) methods to study SEI formation at model anodes with emphasis on additives and electrolyte oxidation at model cathodes.

STATUS OCT 1. 2010: All codes and models except for parameterization of ReaxFF for electrolyte oxidation at cathode surfaces are in place. Initial novel electrolytes and additives of interest were determined, based upon consultation with other BATT investigators. All systems to be studied in investigations of SEI structure, anode charge transfer resistance, cathode charge transfer resistance, electric double layer structure, capacitance and transport were determined and implemented.

EXPECTED STATUS SEP. 30, 2011: All simulations associated with prediction of SEI structure on model anodes, prediction of charge transfer resistance at model cathode and anode interfaces, including whole cell simulations will be completed. Simulation studies of novel electrolytes in collaboration with BATT investigators will be complete. Studies of electrolyte oxidative stability at model cathode interfaces will be finalized.

RELEVANT USABC GOALS: *10-s discharge power:* 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:
(a) Complete investigation of electric double layer structure and charge transfer resistance as a function of electrode potential for model electrodes. (Feb. 11) **On schedule**
(b) Complete investigation of conductivity of novel high voltage electrolytes. (Apr. 11) **On schedule**
(c) Complete study of SEI formation and role of additives for model anodes. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Fluorination of sulfone is of interest as it could decrease the solvent viscosity and further improve its oxidative stability. This would make it an attractive solvent for electrolytes needed for high voltage cathodes. The influence of fluorination of tetramethylsulfone (TMS) solvent on ion transport and ion dissociation in sulfolane/LiTFSI electrolytes was investigated using molecular dynamics (MD) simulations. See figure on the right side for notation.

Partial fluorination of TMS (TMS_{F4}) increased its self-diffusion coefficient at room temperature by 30% while additional fluorination to TMS_{F8} increased the self-diffusion coefficient by 420%. However, perfluorinated TMS_{F8} did not dissociate LiTFSI salt at TMS_{F8}:Li=10, while partially fluorinated TMS_{F4} dissociated LiTFSI salt to the extent simular to a dimethyl carbonate solvent, resulting in an ionicity of 0.12 as shown in the Table below. Here, ionicity is defined as the electrolyte conductivity devided by the conductivity obtained from the Nernst-Einstein relation assuming no ion correlations. Despite the 30% higher TMS_{F4} solvent self-diffusion coefficient compared to TMS, the drop in ionicity resulted in a significantly lower conductivity of TMS_{F4}/LiTFSI compared to TMS/LiTFSI.

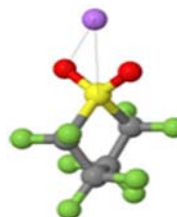|	λ (mS/cm)	D(Li) 10^{-10} m^2/s	ionicity	
TMS/LiTFSI (10:1)	.1	0.35	0	4
TMS_{F4}/LiTFSI (10:1)	0.16	0.13	0.12	
TMS_{F8}/LiTFSI (10:1)	did not dissolve salt			
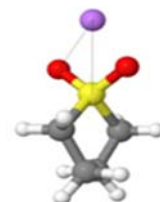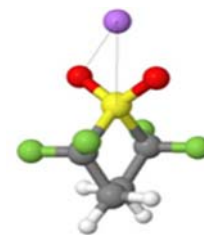
Quantum chemistry studies of the influence of the anion PF_6^- on the oxidative stability and oxidative decomposition pathway of the solvent were performed in collaboration with ARL. Oxidative stability of the PC/PF_6^- complex was found to be reduced compared to the intrinsic oxidative stability of PC solvent, due to the formation of HF upon oxidation of PC/PF_6^-. Importantly, the presence of PF_6^- anion altered the oxidative decomposition pathway of PC and may explain why the solvent reacts at voltages below which previous investigations have predicted.

TASK 3.4 - PI, INSTITUTION: Khalil Amine and Larry Curtiss, Argonne National Laboratory

TASK TITLE - PROJECT: Electrolytes – Advanced Electrolyte and Electrolyte Additives

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Safety, cycle/calendar life, and abuse tolerance

OBJECTIVES: Develop an Advanced Quantum Model to predict functional additives that form stable SEI on carbon anodes and cathodes. Expand model to predict how additives interact with the surface of anode and cathode during initial charging. Synthesize suitable additives predicted by model, characterize and perform extensive cycle and calendar life tests.

GENERAL APPROACH: Search for new electrolytic additives that react in a preferential manner to prevent detrimental decomposition of other cell components. Use quantum chemical screening to predict oxidation and reduction potentials and decomposition pathways that form desirable coatings. Use density functional studies of graphite surface reactions to determine mechanisms for protective film formation from additives.

STATUS OCT 1, 2010: Completed the first phase development of state-of-the-art quantum chemical models to assist in the screening of potential additive candidates by predicting their oxidation and reduction potentials. Initiated refinement of the model and theoretically screened over 100 potential additive molecules.

EXPECTED STATUS SEP. 30, 2010: The promising additive candidates obtained from screening will be further investigated computationally for decomposition products that form a SEI, and testing will be initiated on their performance in a full cell configuration.

RELEVANT USABC GOALS: 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile)

MILESTONES:
(a) Investigate decomposition pathways for the promising additive candidates identified through reduction potential screening and recommend ones for experimental testing. (Apr. 11) **On schedule**
(b) Experimental testing of carbonate-based additive candidates predicted from our computational model. (May 11) **On schedule**
(c) Apply our quantum chemical model for calculation of the oxidation potentials of redox shuttles to predict candidates for experimental testing. (Jul. 11) **On schedule**
d) Calculate structures of SEI components involving carbonates for identification in experimental studies. (Sep. 11) **On schedule**
(e) Carry out quantum chemical studies of feasibility of reaction pathways for polymerization of electrolyte salts. (Sep 11) **On schedule**

PROGRESS TOWARD MILESTONES

The first phase of our work on development of new electrolyte additives for SEI formation involves screening of reduction potentials. As reported previously, the reduction potentials of over 200 candidate materials were calculated using a quantum chemical model based on density functional theory. The second phase involves investigation of the mechanism of decomposition and its relation to the performance of the additive in a battery cell. During the past quarter, a series of promising additives were investigated to try to understand the relationship between performance and possible decomposition products.

Among the promising candidates based on reduction potential screening were lithium tetrafluoro(oxalate) phosphate (LTFOP) and lithium tris(oxalato) phosphate (LTOP). These two compounds were investigated as additives for MCMB/$Li_{1.1}[Ni_{1/3}Co_{1/3}Mn_{1/3}]_{0.9}O_2$ (NCM) cells.
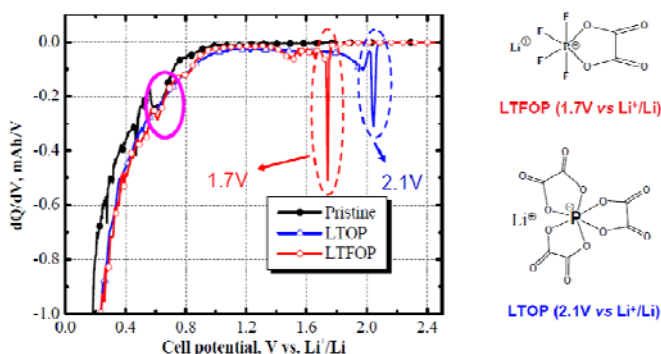

The reduction potentials were measured by charging a Li/MCMB half cell. The reduction peaks shown in Fig. 1 at 1.7 and 2.1 V were observed for LiTFOP and LTOP, respectively, indicating a new SEI formation prior to EC decomposition. The measured reduction peaks were in good agreement with those predicted from our quantum chemical model of 1.52 and 1.88 eV for LTFOP and LTOP, respectively. Based on cell testing, including cycling performance and impedance measurements, the LTFOP additive was found to perform significantly better than the LTOP.

Figure 1. Differential capacity profiles of Li/MCMB with 1.2M $LiPF_6$ EC/EMC 3/7+2% additive.

Possible decomposition reactions for LTFOP were investigated, including (a) opening of the oxalate ring *via* breaking of a P-O bond, (b) decomposition by breaking two P-O bonds to form $C_2O_4^-$ and PF_4^- anions, and (c) decomposition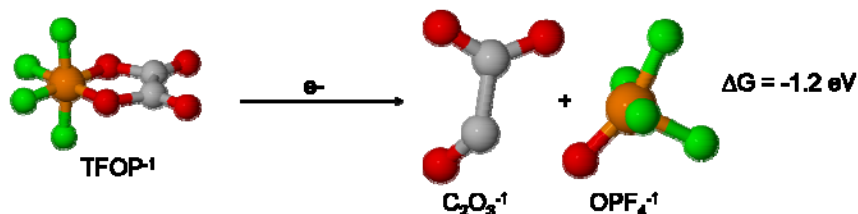 by breaking a P-O bond and a C-O bond on the same ring to form $C_2O_3^-$ and OPF_4^- anions as shown in Fig. 2. In terms of free energies, it was found that all reactions are exothermic with the reaction forming the OPF_4^- anion, was most favorable (Fig. 2). From calculations, the OPF_4^-

Figure 2. Decomposition reaction for tetrafluoro(oxalate) phosphate anion (TFOP) and calculated reaction free energy.

anion was found to form a polymeric species $(OPF_4^{-1})_n$ having linear-type structures. This situation was similar to our studies of lithium difluoro[oxalato]borate (DFOB). In that case, our calculations suggested that DFOB performed better than LiBOB as an additive due to the presence of the fluorines that promoted 2-dimensional SEI film growth as opposed to the 3-dimensional structures formed from the LiBOB.

TASK 3.5 - PI, INSTITUTION: Brett Lucht, University of Rhode Island

TASK TITLE - PROJECT: Electrolytes – Development of Electrolytes for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cell performance, life, cost: Calendar life: 40^oC, 15 yrs; Survival Temp Range: -46 to $+66^oC$; Unassisted Operating & Charging Temperature Range, -30 to $+52^oC$.

OBJECTIVES: Develop novel electrolytes with superior performance to state-of-the art ($LiPF_6$). Develop additives that allow for formation of protective coatings on the cathode, *i.e.*, a cathode SEI, and enhance electrochemical stability above 4.5 V. Develop electrolytes for improved performance of Si-based alloy anodes.

GENERAL APPROACH: Investigate properties of $LiPF_4C_2O_4$/carbonate electrolytes in small Li-ion cells. Investigate electrode surface films for cells cycled with $LiPF_4(C_2O_4)$ to determine source of performance differences. Investigate incorporation of electrolyte SEI forming additives for Si-based Alloy anodes. Investigate cathode film forming additives for high voltage (>4.5 V) cathode materials. Investigate the surface of cathodes and anodes cycled with novel electrolytes, with or without additives, to develop a mechanistic understanding of interface formation and degradation.

STATUS OCT. 1, 2010: Developed cathode film-forming additives that improve the cycling performance of graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells cycled to high voltage (4.8 V *vs* Li). The additives include organic and inorganic species. Expanded our investigation of the novel salt $LiPF_4(C_2O_4)$ by testing it in coin cells under accelerated aging conditions with graphite/ $LiNi_xCo_{1-2x}Mn_xO_2$ cells, and RT cycling of graphite/$LiMn_2O_4$ and graphite/$LiFePO_4$, and graphite/$LiNi_xCo_{1-2x}Mn_xO_2$ cells containing PC.

EXPECTED STATUS SEP. 30, 2011: Will develop additional cathode film-forming additives for high-voltage cathodes, will investigate the low-temperature (-30^oC) performance of $LiPF_4(C_2O_4)$/PC electrolytes after accelerated aging, will develop an understanding of the source of initial capacity fade during formation cycling with $LiPF_4(C_2O_4)$ electrolytes, and will investigate novel electrolytes to improve performance of Si-based alloy anodes.

RELEVANT USABC GOALS: Calendar life: 40^oC, 15 yrs; Survival temp. range: $-46–52^oC$; Cold cranking power at -30^oC; Cycle life; Peak Pulse Discharge Power, 10 sec.

MILESTONES:
(a) Investigate cell performance upon accelerated aging of graphite/ $LiNi_xCo_{1-2x}Mn_xO_2$ cells with $LiPF_4(C_2O_4)$/PC electrolytes compared to $LiPF_6$ electrolytes. (Mar. 11) **On schedule**
(b) Develop improved cathode film forming additives for high-voltage Ni-Mn spinel cathode materials. (Jul. 11) **On schedule**
(c) Develop an understanding of the source of irreversible capacity loss with $LiPF_4(C_2O_4)$ electrolytes during formation cycling. (Jul. 11) **On schedule**
(d) Investigate novel electrolytes to improve performance of Si-alloy anodes. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

With regards to milestone (a): Two classes of additives, inorganic and organic, were investigated that were preferentially oxidized to form a cathode SEI that inhibited the oxidative reactions of the cathode with the electrolyte in $Li/LiNi_{0.5}Mn_{1.5}O_4$ cells. While the incorporation of the additives had only a small effect on the capacity retention of the cells when cycled to 4.9 V *vs.* Li, a significant improvement of the coulombic efficiency was observed. Preliminary investigations indicated that cells containing a standard electrolyte (1.2 M $LiPF_6$ in 3:7 EC:EMC) had efficiencies around 96% during the initial 5 to 10 cycles after formation while cells containing the standard electrolyte with 2% LiBOB had higher efficiencies (98 %).

With regards to milestone (b): investigations of lithium tetrafluorooxalatophosphate ($LiPF_4(C_2O_4)$) in PC-based electrolytes will be expanded. Additional $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$/graphite electrodes were requested to complete these studies. In addition, a temperature chamber was ordered and will arrive in February allowing low-temperature cycling.

With regards to milestone (c): The investigation of $LiPF_4(C_2O_4)$ electrolytes was expanded with a focus on the source of first-cycle irreversible capacity loss. The reversible capacity observed on the formation cycles of cells (MCMB/$LiNi_{0.8}Co_{0.2}O_2$) containing $LiPF_4(C_2O_4)$ electrolytes was 62% as compared to 84% for $LiPF_6$ electrolytes. The differences were suspected to be due to lithium oxalate impurities in the $LiPF_4(C_2O_4)$. Extensive purification of $LiPF_4(C_2O_4)$, followed by cycling of the electrolyte in cells, suggested that the lithium oxalate impurities contributed to the irreversible capacity, but efficiencies in excess of 65% could not be obtained *via* $LiPF_4(C_2O_4)$ purification. However, it was also found that formation cycle efficiencies vary significantly as a function of the electrode materials. Investigation of $LiPF_4(C_2O_4)$ electrolytes in non-MCMB graphite (NG)/$LiFePO_4$ cells provided nearly identical reversible capacities (83%) upon formation. In addition, the cell capacity during the first 50 cycles was slightly better for $LiPF_4(C_2O_4)$ than $LiPF_6$. Related NG/$LiNi_{0.8}Co_{0.2}O_2$ cells and MCMB/$LiFePO_4$ cells were prepared and cycled confirming the source of the efficiency difference as the anode material. Initial surface analysis of the anodes after cycling supported the presence of very similar species on the MCMB and NG (Fig. 1). Further analysis is being conducted to find the source of the differences in first-cycle loss.

With regard to milestone (d): discussions to obtain Si anodes are in progress.
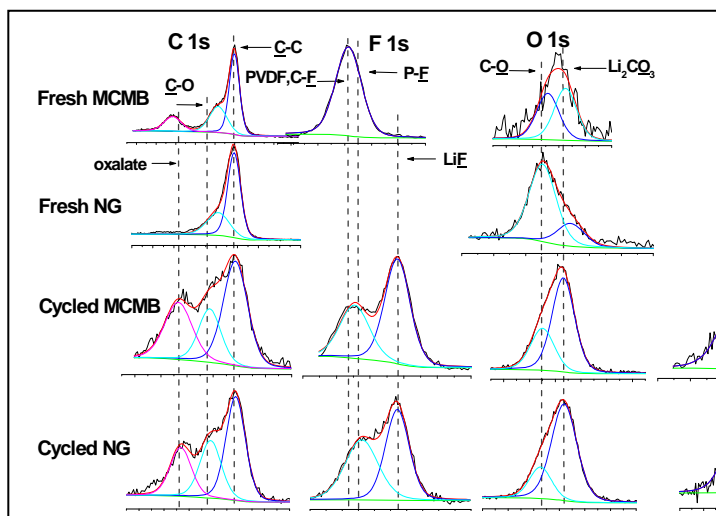
TASK 3.6 - PI, INSTITUTION: Daniel Scherson and John Protasiewicz, Case Western Reserve University

TASK TITLE - PROJECT: Electrolytes – Bifunctional Electrolytes for Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Abuse tolerance

OBJECTIVES: I. Design, synthesize, and characterize physical, electrochemical, and interfacial characteristics of functionalized Li-salt anions containing: **a.** phosphorus moieties known to impart materials with flame retardant properties (Flame Retardant Ions or FRIONs); and **b.** additional functional redox active groups capable of providing overcharge protection, FROPs. These new classes of materials will improve device safety without impairing device performance. **II.** Develop and implement ATR-FTIR spectroscopic methods for monitoring *in situ* the nature of products generated at Li-ion battery anodes under highly-controlled conditions.

GENERAL APPROACH: **I.** Develop methods for the chemical functionalization of anions known to improve the performance of Li-ion batteries with covalently linked groups displaying flame retardant and/or overcharge protection attributes. **II.** Establish guidelines for the rational design and synthesis of optimized FRIONs and FROPs based on the analysis of results of testing in actual Li-ion batteries. **III**. Develop new *in situ* tactics for the application of attenuated total reflection Fourier transform infrared ATR-FTIR for the characterization of solution products generated at Li-ion battery anodes and solid electrolyte interfaces formed therein.

STATUS OCT. 1, 2010: Fully synthesized, purified and characterized first-generation LiBOP-type FRIONs in amounts sufficient for thorough battery testing. Synthesized and preliminarily evaluated several members of the cyclic borate phosphine oxides (CBPO)-type of FRIONs. Preliminary measurements with the newly constructed *in situ* ATR-FTIR cell aimed at monitoring *in situ* the composition of the electrolyte and surface films on ultrapure Li metal electrodeposited *in situ* in the same cell in alkyl carbonate solvent-salt formulations provided by Novolyte Technologies. Completion of flammability tests of first FRION. Submission of first paper to refereed Journal.

EXPECTED STATUS SEP. 30, 2011: Completion of synthesis, purification and characterization of CBPO, a second class of FRIONs, in amounts sufficient for full electrochemical and battery testing. Large scale synthesis and purification of first-class FRIONs for thorough performance assessment in Li-ion batteries. Systematic *in situ* ATR-FTIR spectroscopic studies involving solvent formulations incorporating Case FRIONs as additives.

RELEVANT USABC GOALS: No fire or rapid disassembly of cells during abuse conditions.

MILESTONES:
(a) Prepare and fully characterize three new LiBOP-type FRIONs. (Oct. 10) **Delayed, due Feb. 11**
(b) Prepare and characterize new FRIONS based on properties of LiBOP-type FRIONs. (Jan. 11) **On schedule**
(c) Implement *in situ* ATR-FTIR cell and examine solution phase and SEI for electrolyte formulations with and without first type of FRIONs. (Jan. 11) **On schedule**
(d) Synthesize and characterize completely new class of FRIONs (CBPOs). First example of CBPO will be achieved, and initial evaluation will be accomplished. (Mar. 11) **On schedule**
(e) Characterize and test three (or more) members of CBPO class of FRIONs. (Sep. 11) **On schedule**
(f) Implement *in situ* ATR-FTIR cell and examine solution phase and SEI for electrolyte formulations with and without second type of FRIONs. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

a. Synthesis of FRIONS – In the last quarter, we introduced the design of LiBOBPHO-Ar, a substituted derivative of our original FRION LiBOBPHO-Ph. LiBOBPHO-Ar was prepared, fully characterized, and connectivity established by XRD (Scheme 1). This material has a
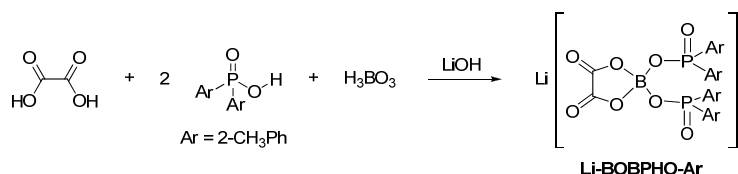

Scheme 1

methyl substituent on each aromatic ring of the phosphinic acid moiety. The substituted phosphinic acids were synthesized from the corresponding Grignard reagent and diethylphosphite and then oxidized. To better understand the behavior of the FRIONS when subjected to fire, heat release testing was performed at the University of Dayton Research Institute (Table 1). Using a micro combustion calorimeter (MCC), our collaborators demonstrated that the LiBOBPHO-Ph and LIBOBPHO-Ar had increased delay times to ignition. Moreover, there was a substantial amount of char formed, which typically corresponds to a decrease in total heat release. The early onset peaks were attributed to the recrystallization solvent, tetrahydrofuran.

Table 1. Heat Release Data.

Sample	Mean Char Yield[a] (wt%)	Mean HRR Peaks[ab] (W/g)	Mean Max T[a] (°C)	MeanTotal HR[ac] (kJ/g)
LiBOBPHO-Ph	23.62(0.02)	49(0.02), 82(0.03), 5(0.1), 225(0.03)	158(0.006), 178(0.006), 298(0.01), 562(0.005)	20.5(0.02)
LiBOBPHO-Ar	20.15(0.03)	125(0.07), 55(0.4), 15(0.2), 287(0.03)	184(0.006), 231(0.002), 336(0.01), 497(0.003)	24.7(0.007)
LiPHO-Ph	7.93(0.04)	26(0.06), 177(0.02), 143(0.06), 150(0.37), 115(0.1), 113(0.02), 109(0.09)	99(0.01), 152(0.003), 402(0.009), 445(0.01), 523(0.009), 643(0.003), 721(0.006)	23.4(0.009)

[a]RDS is parentheses. [b]HRR = Heat Release Rate. [c]Total HR = Total Heat Released.
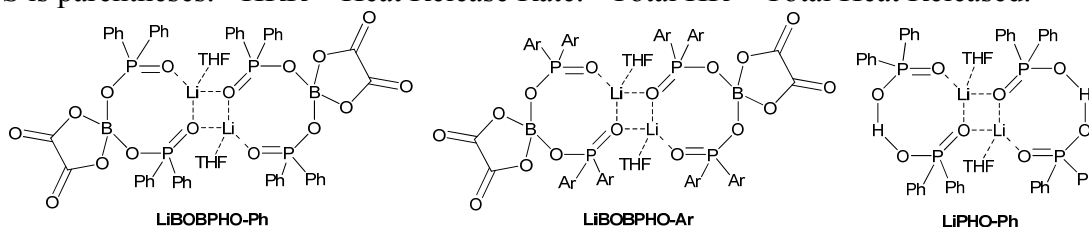
b. Spectroscopic Studies: Attenuated Total Reflection FTIR – Problems were encountered with the original design of the cell, which delayed the start of the proposed measurements. Specifically, the Kalrez o-rings that serve as seals that isolate the inner cell compartment from the ambient atmosphere collapsed following the first few tests. This behavior was attributed to the rather rough finish of the polypropylene body. This problem was recently solved by inserting a glass sleeve press fit onto the PP body, an approach that is showing great promise.

c. Collaborations this quarter – Novolyte agreed to perform tests of materials developed under this program in coin cells. Dr. Alexander Morgan, University of Dayton, will continue performing microcalorimetry tests with materials prepared under this program. These studies will be complemented by TGS, high-resolution mass-spectroscopy to be performed by Dr. Robert Lattimer, Lubrizol Corporation, Strongsville, OH.

TASK 3.7 - PI, INSTITUTION: Wesley Henderson, North Carolina State University

TASK TITLE - PROJECT: Electrolytes – Inexpensive, Nonfluorinated (or Partially-Fluorinated) Anions for Lithium Salts and Ionic Liquids for Lithium Battery Electrolytes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-cost cell materials, abuse tolerance, low-temperature performance

OBJECTIVES: Develop new anions as replacements for PF_6^- or as additives for electrolytes

GENERAL APPROACH: Synthesize and fully characterize two classes of nonfluorinated (or partially-fluorinated) anions: 1) chelated and non-chelated organoborate anions (related to bis(oxalate)borate (BOB^-)), and 2) Hückle-type anions in which the charge is stabilized on a 5-member azole ring and noncyclic cyanocarbanions. Characterize the physical properties of these new anions, incorporated in both Li salts and ionic liquids, by examining the thermal phase behavior (phase diagrams); thermal, chemical, and electrochemical stability; transport properties; interfacial properties; molecular interactions and cell performance. These salts will be compared with widely used salts such as $LiPF_6$ and LiBOB and ionic liquids based upon the bis(trifluoromethanesulfonyl)imide anion.

STATUS OCT. 1, 2010: New salts based upon organoborate and Hückel-type anions were prepared and some of these have been scaled up for extensive characterization. Ionic liquids also were prepared from these anions, and characterized. The phase behavior and properties of solvent-LiBOB and -$LiBF_4$ mixtures were determined for comparison with the new salts to aid in understanding the widely-varying solubility noted for these salts.

EXPECTED STATUS SEP. 30, 2011: Partially-fluorinated anions will have been prepared for comparison with the nonfluorinated salts. These will consist of both fluorine and cyano electron-withdrawing components. The work exploring the solubility and Li^+ cation coordination of organoborate anions in aprotic solvents will provide insight into the selection of these salts as additives to electrolytes.

RELEVANT USABC GOALS: Available energy: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); 10-s discharge power: 750 W/kg (10 mile) and 316 W/kg (40 mile); cycle life: 5000 cycles (10 mile) and 3000 cycles (40 mile); calendar life: 15 years (at 35°C); cold cranking capability to -30°C; abuse tolerance.

MILESTONES:
(a) Characterize the electrochemical properties of lithium dicyanotriazolate (LiDCTA). (Apr. 11) **On schedule**
(b) Synthesize and purify partially-fluorinated cyanocarbanions. (Apr. 11) **On schedule**
(c) Characterize partially-fluorinated cyanocarbanions. (Sep. 11) **On schedule**
(d) Synthesize, purify, and characterize cyanocarbodianions. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Solvent-LiBOB, -LiDFOB and -LiBF₄ Characterization:

The characterization of the thermal phase behavior of binary mixtures of solvent-LiBF$_4$ and LiDFOB (lithium difluoro(oxalato)borate) with nitrile solvents is underway. Mono- and dinitrile solvents have exceptional electrochemical stability and have been demonstrated as potential candidates for high-voltage electrolyte materials. Acetonitrile (AN) was used as a model solvent to better understand the interactions of this solvent with Li salts. AN-LiBF$_4$ mixtures could readily be prepared up to an x = 0.50 (mole fraction) composition. In dilute mixtures, a 4/1 solvent-separated ion pair (SSIP) solvate formed in which four solvent molecules fully coordinated each Li$^+$ cation leaving the BF$_4^-$ anions uncoordinated. More concentrated mixtures formed aggregated (AGG) 2/1 and 1/1 solvates in which the anions were coordinated to two or three Li$^+$ cations, respectively. AN-LiDFOB mixtures, in contrast, formed a 3/1 AGG solvate (Fig. 1a) in dilute mixtures in which the two carbonyl oxygens were coordinated to a Li$^+$ cation (Fig. 1b). The cations were coordinated by two AN molecules and two anions; an uncoordinated AN filled vacancies in the structure. LiDFOB was measured to have a solubility limit of x = 0.29 in AN (much lower than that for LiBF$_4$, but higher than for LiBOB). From more concentrated mixtures, single crystals of a 1/1 AGG solvate grew. The ion coordination in this solvate structure is shown in Fig. 1c. Despite this being a highly aggregated structure, the fluorine atoms of the anion remained uncoordinated (as for the 3/1 solvate). The Li$^+$ cations were coordinated by a single AN and three anions (with four oxygens) resulting in polymeric chains. This extensive polymeric aggregation, even in relatively dilute mixtures due to the oxalate group of the anions, was the likely explanation for the lower solubility of LiDFOB relative to LiBF$_4$ in AN.

Salt and Ionic Liquid (IL) Synthesis:

Synthesis of the cyanocarbanions continues. The salts have not yet been purified for analysis. Synthesis of ILs with the DFOB$^-$ anion is also underway. These ILs cannot be prepared in the same manner as TFSI$^-$-based ILs. Thus, several new preparation procedures are being tested to identify the preferred method for synthesis.

Collaborations this Quarter:
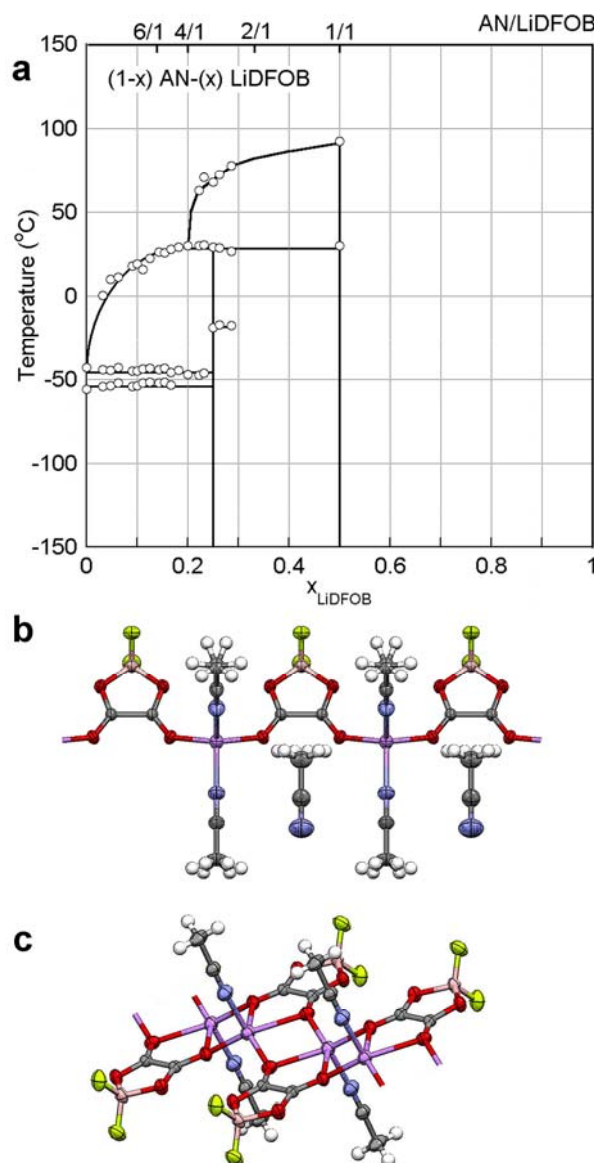
Dr. Richard Jow at the Army Research Laboratory.

Figure 1. (a) Preliminary phase diagram for (1-x) AN-(x) LiDFOB mixtures and ion coordination in the crystal structure of the (b) (AN)$_3$:LiDFOB and (c) (AN)$_1$:LiDFOB solvates (Li: purple, B: tan, O: red, F: green).

TASK 3.8 - PI, INSTITUTION: C. Austen Angell, Arizona State University

TASK TITLE - PROJECT: Electrolytes – Sulfones with Additives as Electrolytes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor abuse tolerance, low energy density, and improved safety.

OBJECTIVES: To devise new electrolyte solvent chemistries that will permit cell operation at high voltages without solvent oxidation and with adequate overcharge protection, and to provide optimized nanoporous supporting membrane for this electrolyte.

GENERAL APPROACH: (i) Design new solvent molecules and solvent mixtures that retain the high-oxidation resistance already demonstrated for noncyclic sulfones while maintaining the solubility of $LiPF_6$ and lowering the liquid viscosity. Included is the determination of how cosolvents will act with ethylmethyl sulfone (EMS) to produce the same effect for mixtures with EMS. (ii) Employ new design principles involving "Maxwell slats" to synthesize nanoporous supports optimized to contain the electrolytes with minimum electrode separation for maximum conductance.

STATUS OCT 1, 2010: Commercially-available methyl sulfonyl fluoride was evaluated, and found uninteresting as a single solvent (because of poor solubility of $LiPF_6$), interesting as a cosolvent with EMS based on conductivity (factor of 3 more conductive than with pure EMS as solvent), but inadequate based on oxidative stability. Likewise for methane sulfonyl chloride which had previously been studied as a single solvent and found to have a wide "window". The latter case has been instructive to demonstrate the lack of synergism of EMS with cosolvents. Where initial experience suggested all co-solvents might experience enhanced stability deriving from the presence of the sulfone, this case proves that it is NOT general, implying that studies of its origin when it occurs, will be desirable. Attempts were made to fluorinate one or more of the ring methylene groups on the known wide window, electrolyte solvent tetramethylene sulfone (sulfolane), for which a substantially-reduced viscosity is predicted.

EXPECTED STATUS SEP. 30, 2011: A substantial number of EMS + cosolvent systems will have been examined, and their $LiPF_6$ dissolving capacities determined, their electrical conductivities examined, and their electrochemical stabilities evaluated. A series of fluorination studies, tested in button cells, will have been carried out and the more promising routes refined. New types of supporting polymers will have been examined and compared with standard cases. These polymer supports will also have been tested for their sequestrating abilities with sulfur as a cathode material in Li-S cells and evaluated for their ability to withstand polysulfide components in the solution.

RELEVANT USABC GOALS: 1000 cycles (80% DoD); 10 year life. An electrolyte with electrochemical window 5.2 volts and conductivity 20 mS/cm.

MILESTONES:
(a) Complete full evaluation of cosolvent systems and determine useful limits. (Dec. 10) **Complete**
(b) Realize first two fluorination objectives or prove inaccessible. (Mar. 11) **On schedule**
(c) Perform preliminary evaluation of "Maxwell slat" nanoporous membrane concept Mar. 11 **On schedule**
(d) Perform advanced evaluation of "Maxwell slat" concept for creation of self-supporting films of nanoporous supporting membrane for sulfone electrolytes. Perform preliminary tests of this medium for isolation of polysulfides in Li-S cells. (July 11) **On schedule**
(e) Realize second two fluorination prospects, or prove them inaccessible. (Jul. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Successful synthesis of a fluorinated sulfolane was reported in 2010, 4th quarter. The electrochemical window was very good and the melting point was lower (0.7ºC *vs.* 18ºC for sulfolane), but the conductivity was lower than sulfolane. The mixture of this new solvent with DMC 1:1 was tested. The conductivity is compared with previous solvents and with other recently tested mixtures in Fig. 1; the electrochemical window is shown in Fig. 2. The conductivity was found to fall below that of the carbonate mixture EC-DMC (1:1) by a factor of three. These results are essentially as predicted by the calculations obtained in *collaboration with Oleg Borodin.*
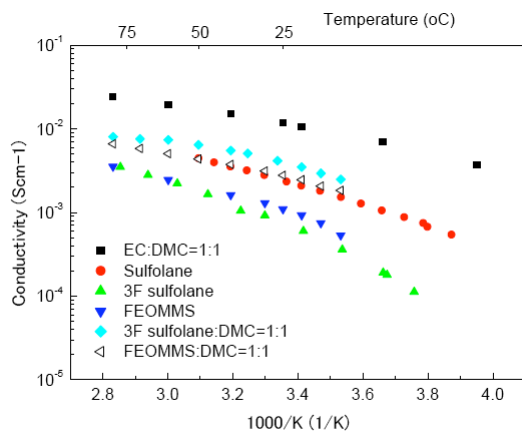

Figure 1. Specific conductivities of 1M LiPF$_6$ solutions in various solvents prepared in this work. FEOMMS is the new fluorinated solvent, described below.
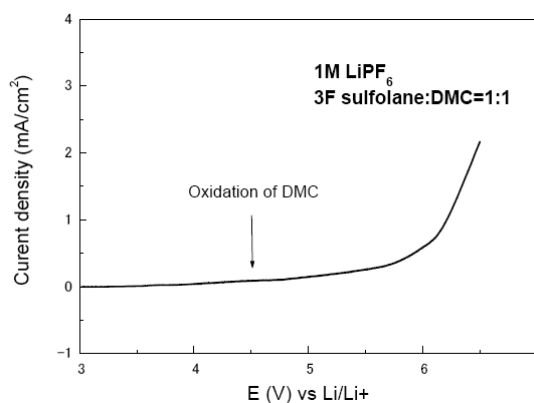

Figure 2. Oxidative stability of the 3-fluorosulfolane-DMC 1:1 solution, showing remarkable high limit at the lithium manganate cathode.

In more recent work, we obtained a second fluorinated sulfone, $CF_3CH_2OCH_2SO_2CH_3$ (FEOMMS), which is a 1,1,1 perfluoromethane version of one of the ethersulfones described recently by Sun and Angell. The conductivity of 1M LiPF$_6$ in this solvent is higher than in 3-fluoro-sulfolane but lower than in sulfolane. Data are included in Fig. 1 above. The electrochemical window for this solvent cannot be assessed until a higher purification is achieved, but the window for 3-fluorosulfolane + DMC(1:1) proved remarkably high, illustrating again the synergism possible in sulfone-carbonate solutions. This will be explored further in the next quarter.
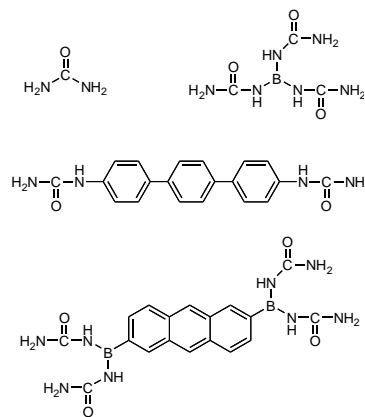
Significant progress has been made in the second and more ambitious component of our program aimed at providing a novel nanoporous molecular net. This will serve as a novel type of confining medium, *i.e.* an anode-cathode separator for high-voltage electrolytes. The first stage of this constraint-theory-based project involved a thermally-reversible assemblage design, using hydrogen-bonded connections that are not suitable for high-voltage systems, but excellent for fixing design parameters. The 3- and 4-linkers for this self-assembling "Maxwell slat glass", based on "sticky" urea (top left) derivatized boron 3-linkers (see top right structure) and silicon 4-linkers (not shown), were prepared and characterized, and the "slats", both flexible (middle structure) and rigid (lower structure), are in final synthetic stages.

It is expected that the success (or otherwise) of this concept for providing assemblages of variable porosity at the nano-level will be established by the next reporting date.

BATT TASK 4
CATHODES

Task 4.1 - PI, INSTITUTION: Michael Thackeray, Argonne National Laboratory

TASK TITLE - PROJECT: Cathodes – Novel Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy, cost, and abuse tolerance limitations of Li-ion batteries

OBJECTIVE: To develop low-cost, high-energy and high-power Mn-oxide-based cathodes.

GENERAL APPROACH: Structurally-integrated $xLi_2MnO_3\bullet(1-x)LiMO_2$ composite structures (M = Mn, Ni and Co) provide exceptionally high-rechargeable capacities (>200 mAh/g) if charged above 4.5 V, which destabilizes the electrode surface, resulting in a first-cycle irreversible capacity loss. Our approach is to design surface architectures that mitigate these performance limitations. In FY2011, we will continue our efforts to 1) stabilize the electrodes at high potentials without compromising rate capability, 2) minimize the need for electrochemical activation, 3) evaluate autogenic reactions to fabricate carbon, metal-oxide, and metal-phosphate coatings, and 4) use atomic simulations to model structural configurations of surface-protected $LiMn_2O_4$ electrodes.

STATUS OCT 1. 2010: Progress was made in enhancing the rate capability of high-capacity $xLi_2MnO_3\bullet(1-x)LiMO_2$ (M=Mn, Ni, Co) electrodes by stabilizing the electrode surface with a lithium-nickel-phosphate coating. Autogenic reactions were successfully used to synthesize and carbon-coat $LiFePO_4$ in a single step. Theoretical studies of the solubility and surface structure of $LiMn_2O_4$ in an acidic medium were extended and completed.

EXPECTED STATUS SEP. 30, 2011: Progress will have been made in enhancing the surface stability of 'layered-layered' $xLi_2M'O_3\bullet(1-x)LiMO_2$ electrodes at high potentials, with improvements in rate capability and cycle life. Methods to overcome the first-cycle capacity loss by minimizing the necessity for electrochemical activation will have been evaluated. Attempts to deposit carbon and stabilizing metal oxide or metal phosphate stabilizing layers on metal oxide electrode surfaces by autogenic reactions will have been made. Theoretical simulations of coated electrode surfaces will have been conducted.

RELEVANT USABC GOALS: 200 Wh/kg (EV requirement); 96 Wh/kg, 316 W/kg, 3000 cycles (PHEV 40 mile requirement). Calendar life: 15 years. Improved abuse tolerance.

MILESTONES:
(a) Engineer, improve, and evaluate the electrochemical properties of stabilized surfaces of composite electrode structures with a high Mn content. (Sep. 11) **On schedule**
(b) Evaluate autogenic processes for coating metal oxide cathode particles with carbon and for fabricating stabilized surfaces with metal oxide and/or phosphate layers. (Sep. 11) **On schedule**
(c) Model coatings and interfacial phenomena at the surface of $LiMn_2O_4$ electrodes. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborators: S.-H. Kang (co-PI), Kevin Gallagher, Donghan Kim
Milestone (a) addressed: Engineer, improve, and evaluate the electrochemical properties and surface stability of composite electrode structures with a high Mn content.

It is now well known that Li- and Mn-rich mixed metal-oxide electrodes with integrated 'layered-layered' $xLi_2MnO_3 \bullet (1-x)LiMO_2$ structures (M=Mn, Ni, Co) can provide exceptionally high rechargeable electrochemical capacities of 240 mAh/g or more if they are initially charged to
4.6 V. This process removes Li_2O from the Li_2MnO_3 ($Li_2O \bullet MnO_2$) component thereby generating an electrochemically-active MnO_2 component within the structure. However, over recent years it has been established that if these composite-electrode structures are continually cycled between 4.6 and 2.5 V, the cell voltage decays during discharge, compromising energy efficiency, cycling stability, and cell performance. Studies were initiated to address this issue [1].

The electrochemical charge/discharge profiles of $Li/0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ cells cycled between 4.6 and 2.0 V at a *ca*. C/15 at room temperature and 55°C are shown in Figs. 1a and 1b, respectively; dQ/dV plots of the high temperature profiles (Fig. 1b) are provided in Fig. 1c. (The dQ/dV plots of room temperature cells were similar to those of high-temperature cells and are not shown because of space limitations). It is clear from these data that, at both room temperature and at 55°C, the discharge voltage was continuously suppressed on cycling, leading to a reduction in cell energy and energy efficiency; the voltage decay occurred more rapidly at 55°C. In particular, the dQ/dV data clearly indicated a gradual shift of the discharge potentials at approximately 3.7 and 3.3 V to approximately 2.9 V after 50 cycles. Although the reasons for this behavior are not yet fully understood, the change in the electrochemical profiles strongly suggests that activation of the $0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ electrode at 4.6 V and continued cycling to this high charging potential was likely accompanied by migration of Mn and Ni ions from the transition metal layers to the Li layers, yielding a complex, composite structure in which spinel-like components become embedded within the layered component of the parent structure. Work is in progress to obtain a better understanding of the processes involved and to find solutions to overcoming these internal phase transitions through modifications to both the bulk and surface compositions.
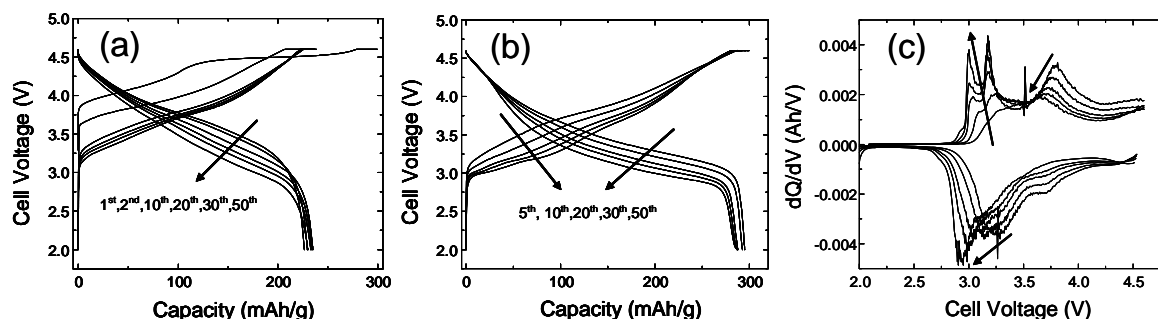

Figure 1. Voltage profiles of $Li/0.5Li_2MnO_3 \bullet 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ cells cycled between 4.6 and 2.0 V, ~C/15 rate, at (a) room temperature, and (b) 55 °C; (c) dQ/dV plots of (b).

Reference

1. K. G. Gallagher, D. Kim and S.-H. Kang, Abstr. 993, 218th Electrochem. Soc. Meeting, Las Vegas, 10-15 October, 2010.

TASK 4.2 - PI, INSTITUTION: M. Stanley Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes - Materials – Novel Cathodes

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg (700-800 Wh/kg), and (b) moderate-rate PHEV compatible cathodes, both of which are based on environmentally-benign materials.

GENERAL APPROACH: Our cathode approach is to place emphasis on low cost oxides and phosphates, both pure and modified with other transition metals, using a range of practical synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2010: For the $LiFePO_4$ olivine, it was determined that the rate capability can be improved by substituting *ca.* 5% of another ion such as vanadium or magnesium. This is believed to be due to a reduction of the nucleation energy for formation of the second phase. Such substitution also substantially enhances the volumetric capacity, by minimizing the amount of carbon conductor. It was also shown that the olivines can be formed hydrothermally. For the layered metal dioxides, we have determined that they can be structurally stabilized with around 3% Ni in the Li layer, that no more than 20% Co is required to achieve optimum capacity at rates exceeding 2C, and that charging potentials in excess of 4.3 V are required to achieve discharge capacities exceeding 200 Wh/kg. Candidate materials that allow for more than one electron reduction per transition metal were identified.
• $LiFePO_4$: > 120 Ah/kg for 100 cycles at 1 mA/cm^2 (1C rate).
• Layered $Li_xCo_zNi_yMn_{1-y-z}O_2$: 160 Ah/kg and 150 Ah/kg for 60 cycles at 1 and 2 mA/cm^2 respectively.

EXPECTED STATUS SEP. 30, 2011: For low-cost Li-Ion cells, we expect to identify the $Li_xMn_{1-y-z}Ni_yCo_zO_2$ systems that have the potential to achieve over 200 Ah/kg at a C rate. Emphasis will be placed on the $Li_xMn_{0.4}Ni_{0.4}Co_yM_{0.2-y}O_2$ compositions. We will have extended our studies beyond olivine-structured lithium-metal phosphate and evaluated some manganese-containing iron phosphates (non-olivine). We also will have explored some higher-capacity, next-generation cathodes, including some based on vanadium.

RELEVANT USABC GOALS: 5000 deep and 300,000 shallow discharge cycles, and lower cost batteries.

MILESTONES:
(a) Identify $LiNi_yMn_yCo_{1-2y}O_2$ systems that can achieve 200 Ah/kg for PHEV applications. (Mar. 11) **On schedule**
(b) Identify and evaluate phosphate structures, containing Fe and/or Mn that have the potential of achieving an energy density exceeding 700 Wh/kg. (Sep. 11) **On schedule**
(c) Identify other materials, including those containing vanadium, that can undergo more than one electron transfer per redox center (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Milestone (a) is reported below. Work on milestones (b) and (c) is underway, and the initial results, performed jointly with G. Ceder at MIT, were just published; (1) below.

Layered Transition Metal Oxides. The rate capability of the NMC, $LiNi_yMn_yCo_{1-2y}O_2$, was evaluated in two different cell configurations. In the first, the NMC for y =0.5 and 0.333 was mixed with different amounts of carbon to evaluate the impact of electrode conductivity and dilution of active material. The results for cells charged up to 4.3 V at a C/10 rate are shown in Fig. 1. The data clearly indicate that indeed added carbon had a marked positive effect on the capacity of the active material. They also indicate that the Co-containing material had superior performance at all rates above 0.1C. In the second cell configuration, expanding on joint studies with C. Ban and A. Dillon, NREL, reported last quarter, the capacity as a function of rate for NMC supported on a carbon nanotube grid was determined. The results are shown in Fig. 2 for 0, 20 and 33.3 at% Co content. The graph indicates that the 442 composition was comparable to the standard 333 composition and superior to 550. At very low rates, the 442 composition had the highest capacity. Some of this joint work with NREL was just published; see (2) below.
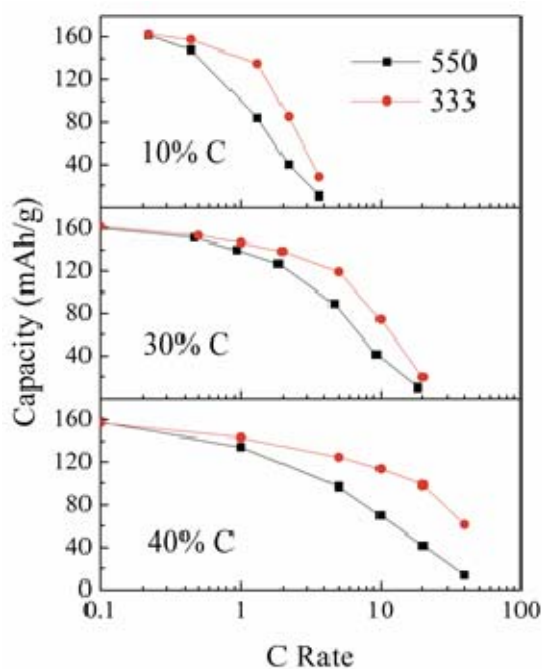

Figure 1. Shows the Ragone plot of 333 and 550 using different amounts of carbon black of 10, 30, and 40 wt%. 10 wt% binder was used for all electrodes. The cells were charged at 0.1C to 4.3 V and held at constant voltage for 6 hours before discharge at various currents.
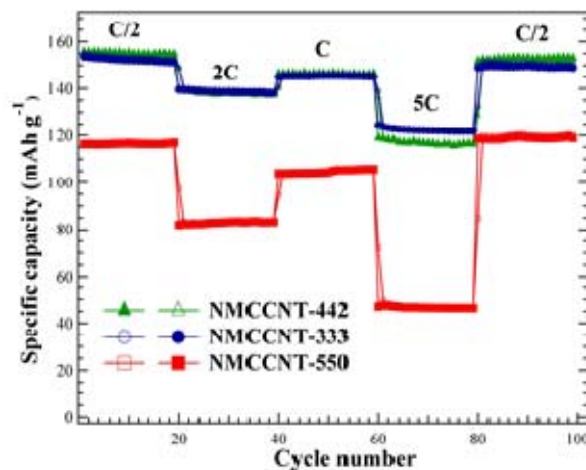
Figure 2. The cycling performance of the carbon nanotube supported NMC: $LiNi_yMn_yCo_{1-2y}O_2$.

Next quarter, the result of studies to understand the cause of the first cycle loss will be reported.

Publications and Presentations

(1) Hui Zhou, Shailesh Upreti, Natasha A. Chernova, Geoffroy Hautier, Gerbrand Ceder, and M. Stanley Whittingham, "Iron and Manganese Pyrophosphates as Cathodes for Lithium Ion Batteries," *Chemistry of Materials*, 2011, 23: 293-300.
(2) Chunmei Ban, Zheng Li, Zhuangchun Wu, Melanie J. Kirkham, Le Chen, Yoon Seok Jung, E. Andrew Payzant, Yanfa Yan, M. Stanley Whittingham, and Anne C. Dillon, "Extremely Durable High-Rate Capability of a $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ Cathode Enabled by Single–Wall Carbon Nanotubes," *Advanced Energy Materials*, 2011, 1: 58-62.

TASK 4.3 - PI, INSTITUTION: Marca Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes – Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-ion Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, power and/or energy density, cycle life

OBJECTIVES: To develop low-cost benign cathode materials having electrochemical characteristics (*e.g.,* cycle life, energy and power densities) consistent with the USABC goals.

GENERAL APPROACH: Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed towards surveying new materials with potential for increased energy density.

STATUS OCT 1. 2010: Electrochemical characterization of the $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ (992) system was carried out this year. Aluminum substitution had little negative impact on the practical capacity and better cycling was achieved than for unsubstituted compounds, but no rate enhancement effect was observed. A systematic investigation of the effect of Ti substitution for Co in NMCs continues. Ti-substituted materials have increased electrochemical capacity compared to the unsubstituted compounds, but the mechanism remains unclear. A spray pyrolysis setup for synthesis of metal oxides and polyanionic composites with carbon has been optimized.

EXPECTED STATUS SEP. 30, 2011: Further investigations into the effect of Ti and Al substitution on NMCs will be carried out. This includes electrochemical and structural characterization in conjunction with other members of the BATT program (Cabana, Persson, Richardson, Chen). The spray pyrolysis system will be modified so that smaller particles can be produced.

RELEVANT USABC GOALS: High power, low cost (HEV). High energy, low cost, cycle life (EV, PHEV).

MILESTONES:
(a) Complete structural and electrochemical characterization of $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ system. (Jun. 11) **On schedule**
(b) Finish survey of Ti-substituted NMCs and select most promising materials for further study. (Jun. 11) **On schedule**
(c) Decrease particle size of polyanionic compound/C composites prepared by spray pyrolysis. Investigate synthesis of new materials by this method and others for comparison. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

a) *(Li[Ni$_{0.45}$Co$_{0.1-y}$Al$_y$Mn$_{0.45}$]O$_2$ system)* Several Li half cells containing Li[Ni$_{0.45}$Co$_{0.1-y}$Al$_y$Mn$_{0.45}$]O$_2$ electrodes were cycled at 0.1 mA/cm^2 between 4.7 (50 cycles) or 4.3 (120 cycles) and 2.0V. All cells exhibited some fading. XRD patterns were obtained on electrodes recovered from these cells in the fully-discharged state. Unit cell parameters and volumes had increased slightly after cycling for all samples (Fig. 1). Cell volumes and the *a* parameter decreased during delithiation of these materials, so these changes could not be explained solely by incomplete recharging due to the capacity fade. Instead, these results implied a structural change, which may have been responsible for the capacity losses. High-resolution synchrotron XRD experiments at the Argonne Advanced Photon Source are planned to investigate this phenomenon further (with J. Cabana, LBNL).

b) *(Ti-substituted NMCs)* Charge compensation must occur when Ti is substituted for Co. This can take place *via* co-substitution with Li on *3b* sites, resulting in Li excess materials. These materials exhibit increased capacity after initial charge to high voltages, as is seen with layered-layered composites and other Li-excess NMCs. Stoichiometric Ti-substituted materials could also be synthesized (although the solid solution range is limited), where charge compensation occurred either by Li deficiencies in *3a* sites or by reduction of some Mn^{4+} to Mn^{3+}. This type of material showed increased discharge capacities compared to the baseline NMC due to lower first-cycle inefficiencies. It was speculated that the introduction of mixed transition-metal oxidation states in the fully lithiated state improved the conductivity, which in turn, aided the transport near the end of discharge. Magnetic measurements and DC conductivity experiments are planned to test this theory. *J. Mater. Chem* has recently accepted our paper on this topic.

c) *(Spray pyrolysis)* High-performance LiFePO$_4$/C and LiCoPO$_4$/C composites were successfully synthesized and two publications are in preparation (with T. Richardson, LBNL). However, our attempts to produce a good sample of LiMnPO$_4$/C failed, and no further work on this material is planned. Instead, the high-voltage spinel, LiNi$_{0.45}$Mn$_{1.55}$O$_4$ (LNMS), was prepared by spray pyrolysis of aqueous nitrate precursors (Fig. 2). LNMS produced by this method will be subjected to various thermal treatments to improve crystallinity and increase grain size, and will be characterized electrochemically.
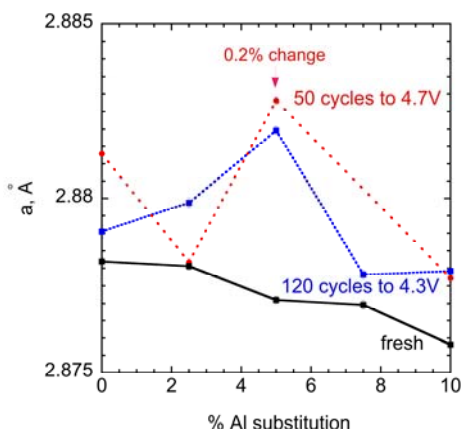

Figure 1. Changes in the *a* unit cell parameters of Li[Ni$_{0.45}$Co$_{0.1-y}$Al$_y$Mn$_{0.45}$]O$_2$ materials after cycling.
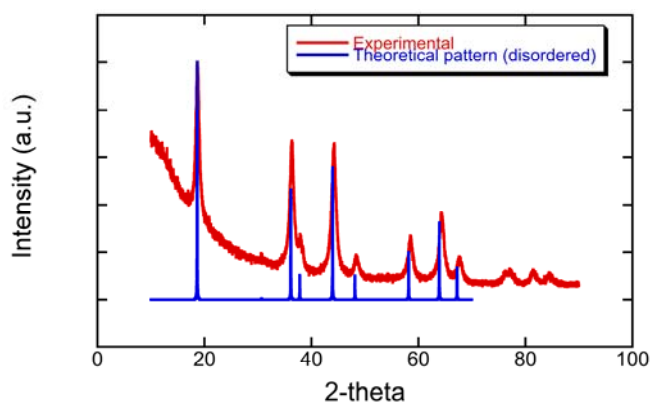
Figure 2. XRD pattern of LiNi$_{0.45}$Mn$_{1.55}$O$_4$ prepared by spray pyrolysis, prior to thermal treatment.

TASK 4.4 - PI, INSTITUTION: Arumugam Manthiram, The University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – High-Performance Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Cost, energy density, power density, cycle life, and safety

OBJECTIVES: To develop (i) low-cost spinel oxide compositions that can offer high energy and power, excellent cycle life, good storage characteristics, and good safety, and (ii) low-cost cathodes based on polyanions that can offer a combination of high energy and power with excellent thermal stability and safety.

GENERAL APPROACH: Our approach is to continue to develop a firm scientific understanding of the factors that control/influence the electrochemical performances of the cathodes and utilize the knowledge gained to design and develop high-performance spinel and polyanion-containing cathode compositions. In this regard, (i) cationic and anionic substitutions and surface modifications of spinel oxide cathodes, and (ii) novel cathodes consisting of polyanions are being pursued. Particularly, (i) self-segregation of certain substituted cations to the surface during the synthesis process that can suppress metal ion dissolution from the cathodes and/or control the SEI layer formation in high voltage (~ 4.7 V) spinel cathodes and (ii) novel synthesis approaches for polyanion-containing cathodes are investigated. Conventional ceramic synthesis and innovative synthesis approaches, such as microwave-assisted solvothermal methods that can offer controlled nanomorphologies, advanced chemical and structural characterizations, and electrochemical evaluation with Li and carbon anodes are being pursued. Based on the characterization data gathered, a fundamental understanding of structure-composition-property-performance relationships will be developed.

STATUS OCT 1. 2010: Developed (i) stabilized 4 and 5 V spinel cathode compositions through self-surface segregation and chemical-surface modifications, (ii) microwave-assisted solvothermal and template-assisted syntheses of cathodes based on polyanions with nanorod and nanowire morphologies, and (iii) an understanding of their structure-composition-property-performance relationships.

EXPECTED STATUS SEP. 30, 2011: Development of (i) an understanding of the self-surface segregation of cations during the synthesis process of high-voltage (4.7 V) spinel oxide cathodes through advanced characterization methodologies, (ii) novel solution-based synthesis approaches to obtain high-capacity nanostructured polyanion (silicate and phosphate) cathodes, and (iii) an understanding of their structure-composition-property-performance relationships.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, 10-year life, <20% capacity fade over a 10-year period

MILESTONES:
(a) Understand self-surface segregation of cations in high-voltage spinel cathodes. (Mar. 11) **On schedule**
(b) Develop novel synthesis approaches for high-capacity nanostructured silicate and phosphate cathodes. (Sep. 10) **On schedule**

PROGRESS TOWARD MILESTONES

With an aim to increase energy and power densities, the spinel cathodes based on $LiMn_{1.5}Ni_{0.5}O_4$ have become appealing due to their high operating voltage of *ca*. 4.7 V with a capacity of *ca*. 130 mAh/g. However, the major issues with this high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathode are the (i) formation of a $Ni_{1-x}Li_xO$ impurity phase, (ii) cationic ordering between Mn^{4+} and Ni^{2+}, resulting in low rate capability, and (iii) chemical instability of the cathode surface in contact with the liquid electrolytes and the consequent formation of a thick (SEI) layer. Based on XRD and FTIR data, it has been shown that the $Ni_{1-x}Li_xO$ impurity phase can be eliminated and a spinel phase with a disordering of Mn^{4+} and Ni^{2+} can be obtained by cationic substitutions for Mn or Ni, or both. It has also been shown that the chemical instability of the cathode in contact with the electrolyte and the formation of SEI layer could be suppressed by a coating of the cathode surface. Two examples include inert oxides, like Al_2O_3 or $AlPO_4$, added by a post-chemical process and a segregation of certain cations, such as Fe^{3+} in $LiMn_{1.5}Ni_{0.5-y}Fe_yO_4$, to the surface during the synthesis process. The coatings provide a more stable cathode-electrolyte interface as indicated by XPS data. The cationic substitutions, chemical coating, and surface segregation were all found to lead to much better cycle life and rate capability compared to the pristine $LiMn_{1.5}Ni_{0.5}O_4$.

The aim this quarter was to develop an understanding of the influence of particle size, shape, morphology, and surface structure on the tap density and the electrochemical performance, such as reversible capacity, cycle life, rate capability, and rate-capability retention during cycling. In so doing, the focus was on the synthesis of the $LiMn_{1.5}Ni_{0.5}O_4$-based spinel cathodes by various solution-based synthesis processes. Specifically, the focus was on the controlled synthesis of materials derived from mixed-metal hydroxide, carbonate, bicarbonate, oxalate, and urea precursors and their characterization by XRD, SEM, TEM, and TGA. It was found that the reaction pH, reaction time, and reactant concentrations played a critical role in controlling the particle size, shape, and morphology.

Figure 1 shows the SEM of the oxalate precursor, the XRD data of the oxalate precursor, and the resulting spinel phase obtained by heating the precursor with LiOH at $850^{\circ}C$. Figure 2 shows the SEM of the carbonate, bicarbonate, and urea precursors that have different sizes and morphologies. In particular, the urea precursor has a microcube morphology, which could be beneficial to increasing the tap density and minimizing the side reactions. Further work is in progress to correlate the data. In addition, preliminary DSC data indicated that the charged $LiMn_{1.5}Ni_{0.5}O_4$ spinel cathodes had lower thermal stability than the charged 4 V spinel cathodes.

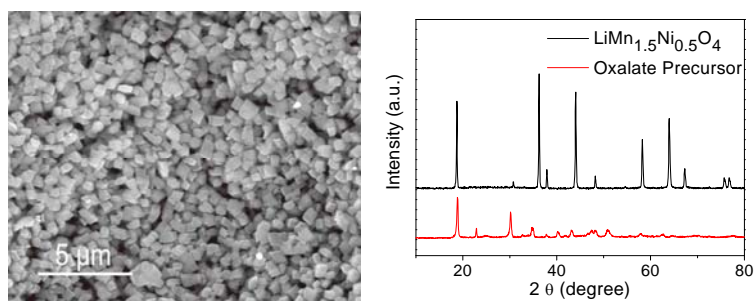**Figure 1.** SEM of the $Mn_{0.75}Ni_{0.25}C_2O_4$ precursor and the XRD of the $Mn_{0.75}Ni_{0.25}C_2O_4$ precursor and $LiMn_{1.5}Ni_{0.5}O_4$ spinel.

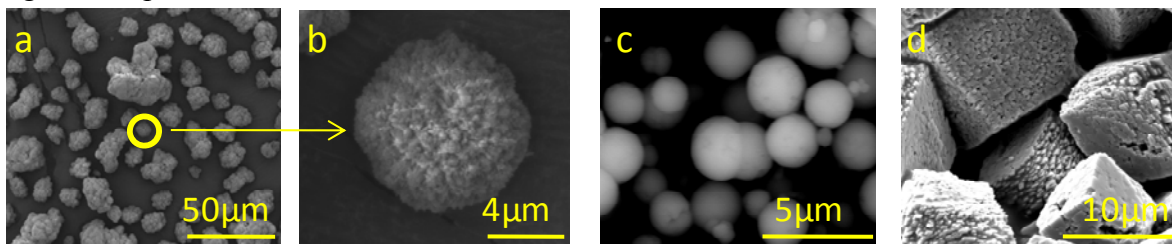**Figure 2.** SEM of the (a) $Mn_{0.75}Ni_{0.25}$ carbonate precursor, (b) $Mn_{0.75}Ni_{0.25}$ carbonate precursor at a larger magnification, (c) $Mn_{0.75}Ni_{0.25}$ bicarbonate precursor, and (d) $Mn_{0.75}Ni_{0.25}$ urea precursor.

TASK 4.5 - PI, INSTITUTION: Ji-Guang (Jason) Zhang and Jun Liu, Pacific Northwest National Laboratory

TASK TITLE - PROJECT: Cathodes – Development of High Energy Cathode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy density, cost, cycle life

OBJECTIVES: To develop high-energy, low-cost, and long-life cathode materials.

GENERAL APPROACH: Our approach is to develop high-energy cathode materials using a nano-engineered synthesis process in combination with the surface treatment and optimization of electrolytes/additives. High-voltage $LiNi_{0.5}Mn_{1.5}O_4$ cathode with surface coating will be investigated using a high-voltage electrolyte. The thermal stability of $LiMn_{1-x}Fe_xPO_4$ will be investigated to validate its feasibility for PHEV applications. Alternative cathodes, such as high rate (up to 30C) $Li_3V_2(PO_4)_3$/C and renewable organic cathodes that exhibit two or more electrons per redox center, will also be evaluated as PHEV/EV compatible cathode materials.

STATUS Oct. 1, 2010: Nanoplates of $LiMnPO_4$ were prepared by a single-step, solid-state reaction with molten hydrocarbon and exhibit a reversible capacity of ~168 mAh/g. A novel cathode material, Li_2CoPO_4F, was synthesized and characterized. Up to 1 mole of Li^+ ions is reversible in Li_2CoPO_4F within 2.0 to 5.5 V. Organic cathodes allowing multiple electron transportation per redox center were prepared with a reversible capacity of more than 200 mAh/g. High-voltage $LiNi_{0.5}Mn_{1.5}O_4$ with a reversible capacity ~130 mAh/g was successfully synthesized with a cost-effective approach suitable for mass production.

EXPECTED STATUS SEP. 30, 2011: The thermal stability of iron-doped $LiMnPO_4$ will be evaluated. The investigation of the electrochemical performance of non-stoichiometric $LiMnPO_4$ will be completed. The coulombic efficiency and cycle life of high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ will be improved by using high-voltage electrolytes/additives and appropriate surface coatings. The performance of a high-rate $Li_3V_2(PO_4)_3$/carbon composite will be investigated. Anthraquinone-based polymer cathode materials will be synthesized, and their operational voltage of this high-capacity material will be tuned by adjusting the functional groups to further improve its energy density.

RELEVANT USABC GOALS: >96 Wh/kg (PHEVs), 5000 deep-discharge cycles, 15-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

MILESTONES:
(a) Evaluate thermal stability of iron-doped $LiMnPO_4$. (Mar. 11) **On schedule**
(b) Synthesize and characterize the high-rate $Li_3V_2(PO_4)_3$/carbon composite. (Jun. 11) **On schedule**
(c) Identify the compatible electrolyte/additive and develop an appropriate surface-coating for the high-voltage cathode, $LiNi_{0.5}Mn_{1.5}O_4$. (Sep. 11) **On schedule**
(d) Synthesize and characterize high-capacity organic cathodes based on the quinonyl group. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

The thermal stability of delithiated $LiMnPO_4$ was systematically investigated at PNNL during the last quarter. $LiMnPO_4$ nanoplate cathode was synthesized by a molten hydrocarbon route. The electrode was prepared by ball milling $LiMnPO_4$ nanoplate with Ketjen black for 4 h followed by mixing with PTFE powders. The obtained composite mixture was rolled into a paper electrode by adding a small amount of isopropanol. The thermal stability of the fresh samples and electrochemically delithiated samples was investigated.

Figure 1 (a) and (b) shows the thermogravimetric analyses (TGA) of a $LiMnPO_4$ electrode before and after electrochemical cycling and the voltage profile of the $LiMnPO_4$ paper electrode (20 to 30 mg/cm^2), respectively. Similar weight losses in the TGA plots were observed for the room temperature and 400^oC samples for both the charged and discharged $LiMnPO_4$ electrodes. EDX analysis of these samples revealed a significant increase in fluorine content after delithiation, which is a clear sign of SEI layer formation. Further investigation by hot-stage, *in situ* XRD (from 30 to 600^oC) showed that the decomposition of $MnPO_4$ into $Mn_2P_2O_7$ occurred at around 450^oC, which is very close to the simulation results reported by Ceder's group. This combination of results indicates that the weight loss shown in the TGA curves between room temperature and 400^oC is due to the decomposition of the SEI layer formed during electrochemical cycling and not to oxygen release from the $LiMnPO_4$ bulk material.

In the next quarter, further characterization using TGA-DSC-MS will be conducted for a more accurate evaluation of the phase change and thermal instability of charged $MnPO_4$, as the gas species evolved during the decomposition will be analyzed.
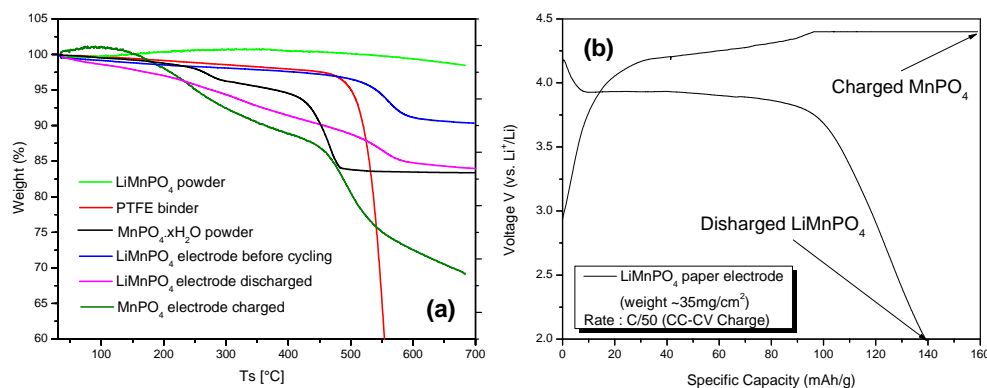

Figure 1. (a) Thermogravimetric analysis (TGA) measurements of the charged and the discharged $LiMnPO_4$ paper electrode under UHP-Ar and (b) charge-discharge voltage profile of $LiMnPO_4$ paper electrode.

Publications:
1. A. Pan, D. Choi, J. Liu, Z. Nie, G. Cao, J. Zhang, J. Xiao, B. W. Arey and S.-Q. Liang, "High-Rate Cathodes Based on $Li_3V_2(PO_4)_3$ Nanobelts Prepared via Surfactant-Assisted Fabrication," *J. Power Sources*. 196 (2011) 3646–3649.
2. A. Pan, J. Liu, J.-G. Zhang, G. Cao, W. Xu, Z. Nie, J. Xiao, D. Choi, B. W. Arey, C. Wang and S. Liang, "Template Free Synthesis of LiV_3O_8 Nanorods as a Cathode Material for High-rate Secondary Lithium Batteries," *J. Mater. Chem.*, 21, p.1153-1161 (2011).

TASK 4.6 - PI, INSTITUTION: John B. Goodenough, The University of Texas at Austin

TASK TITLE - PROJECT: Cathodes – Liquid Cathode Batteries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Stable solid electrolyte with $\sigma_{Li} > 10^{-4}$ S/cm

OBJECTIVE: To explore use of an existing solid Li^+-ion electrolyte with $\sigma_{Li} > 10^{-4}$ S/cm that, though unstable in contact with an acidic aqueous cathode solution, may be stable in a non-acidic solution or if coated with a protective layer. By stabilizing the electrolyte against degradation, which we have shown to be due to the presence of Ti(IV) in the available electrolyte, we can obtain data on the specific capacity versus molar fraction of the Fe^{3+}/Fe^{2+} couple in the cathode solution and how capacity is retained at higher discharge/charge rates. We can obtain data on the ability of seals to prevent water crossover into the anode compartment and on different cathode current-collector configurations. We will also explore composite polymer/inorganic Li^+-ion solid electrolytes in order to develop thin, tough, flexible membranes in collaboration with a polymer chemist. This approach to an alternative cathode can be realized with either a Li^+-ion or a Na^+-ion solid electrolyte, and a search for an alternative solid electrolyte will be made.

GENERAL APPROACH: Exploration of limitations of an aqueous Fe(II)/Fe(III) cathode and of Li^+ and Na^+ solid electrolytes.

STATUS OCT. 1, 2010: A test cell and seals were constructed with the existing commercially-available Li^+-ion electrolyte $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$. The stability of the electrolyte versus a non-acid aqueous solution for the Fe^{3+}/Fe^{2+} couple was tested.

EXPECTED STATUS SEP. 30, 2011: The concept of a liquid-cathode battery with the existing commercial solid electrolyte will have explored more fully. A possible polymer/inorganic-solid composite will be examined as a viable thin, tough, flexible solid-electrolyte membrane. Investigations will be initiated on alternative materials for the Li^+-ion or Na^+-ion solid electrolytes.

RELEVANT USABC GOALS: Available specific energy density > 80 Wh/kg, 5000 deep-discharge cycles, 15-year calendar life.

MILESTONES:
(a) Test liquid-cathode Li battery in which the pH of the cathode solution is alkaline. (Feb. 11) **Complete**
(b) Test a composite Li^+-ion solid electrolyte. (Feb. 11) **On schedule**
(c) Test feasibility of coating the existing solid electrolyte with a protective coat against reduction by an acidic solution. (May 11) **On schedule**
(d) Identify a new Li^+-ion or Na^+-ion solid electrolyte. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

The $Fe(NO_3)_3$ solution as the cathode in a lithium|aqueous-cathode battery (LAB) has been reported. However, the change in the pH of the solution during the charge/discharge process resulted in the formation of precipitates that deteriorated the performance of the LAB. Therefore, a search was initiated for other aqueous cathodes to substitute for the Fe^{3+}/Fe^{2+} couple.

Figure 1 demonstrates the selection strategy for aqueous cathodes for LABs. Aqueous electrodes must have: 1) proper redox potentials; 2) no side reactions; 3) good stability in water; 4) good reversibility; 5) reliable safety; and 6) low cost. Considering the stability of the solid electrolyte $(Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3)$ and the water, the aqueous cathode was restricted to a voltage range of 2.8 to 4.2 V *vs.* Li^+/Li (-0.2 to 1.2 V *vs.* SHE). The voltage range narrowed the selection of cathode redox couples listed in Fig. 1. Tin ions are not stable in water solution and the Cr- and Pb-based redox couples lie outside of the acceptable voltage range, so they were excluded from the candidates of aqueous electrodes. As for Cu- and Mn-based redox couples, side reactions either decrease the operating potential range or damage the aqueous current collectors. Copper ions can be reduced to metallic Cu at a relatively high potential, which decreases the battery performance, and the reaction $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2\downarrow + 4OH^-$ takes place at 0.6V *vs.* SHE to stop the work of MnO_4^-/MnO_4^{2-} and MnO_4^{2-}/MnO_4^{3-}. The formation of MnO_2 precipitate would destroy the reversibility of the battery. Therefore, research was focused on the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple that is very stable in alkaline solutions.

The thermodynamic potential of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ is 0.36 V *vs.* SHE, so the $Li|Fe(CN)_6^{3-}$ (aq) battery presents a voltage of 3.40 V. Figure 2 shows its electrochemical behavior tested between 3.0 and 3.75 V. The effective voltage of the battery distributes between 3.33 and 3.68 V at a current of 0.5 mA/cm^2. The change in ratio of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ leads to the gradient of the charge/discharge curves. The gap between discharge/charge curves of the $Li|Fe(CN)_6^{3-}$ (aq) battery is much smaller than that of a Li/air battery. Unlike the solid electrode materials, the aqueous cathodes do not show any phase changes during charge/discharge, resulting in a high columbic efficiency (CE) and capacity retention for LABs. As for the $Li|Fe(CN)_6^{3-}$ (aq) battery in particular, it showed a CE of 96% at the 20th cycle and no loss in capacity with the $Fe(CN)_6^{3-}$ concentration starting at 0.1 M.
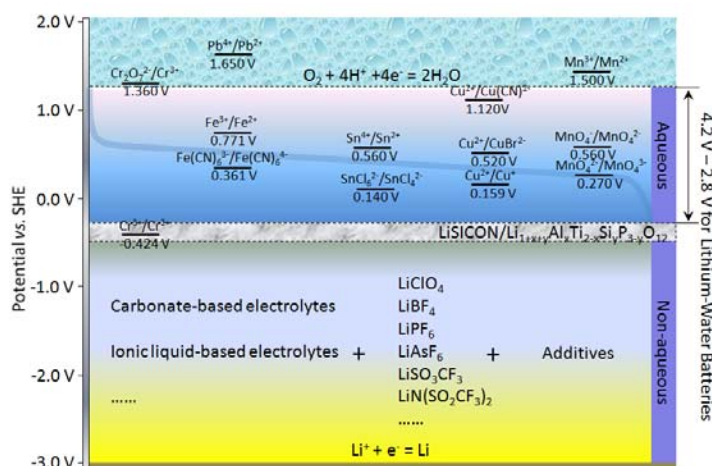

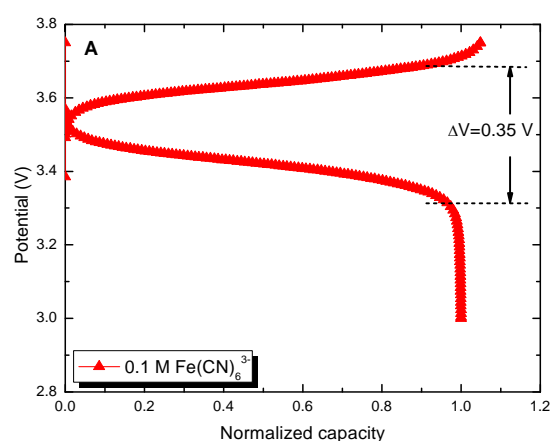**Figure 1.** Selection strategy of aqeous cathodes for LABs.

Figure 2. Charge/discharge curves of the $Li|Fe(CN)_6^{3-}$ battery at the 20th cycle.

TASK 4.7 - PI, INSTITUTION: Jordi Cabana, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes – Positive and Negative Electrodes: Novel and Optimized Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low-energy-density, poor cycle life, safety.

OBJECTIVES: Understand the relationship between particle size-shape and electrode performance. Understand the structure-composition-properties relationship for high voltage spinel electrodes. Understand the chemical and physical phenomena behind the reactivity of negative electrode materials based on metal oxides. Design materials that yield high capacities upon extended cycling.

GENERAL APPROACH: Employ synthesis methods that lead to well controlled particle sizes and shapes, and explore the effect of reaction conditions on the final composition and microstructure. Evaluate changes in properties and morphology upon cycling, and correlate them with the micro and crystal structural features. Use several characterization techniques (diffraction, spectroscopy, microscopy, electroanalysis) to get a complete picture of the different reactions involved in lithium-ion battery electrodes (intercalation, conversion, alloying). .

STATUS OCT. 1, 2010: The performance of $LiNi_{1/2}Mn_{3/2}O_4$ made using solvothermal routes was evaluated. Nanometric Sn particles showing narrow size and shape distributions were prepared and tested. The conversion reaction of NiO was studied by Li NMR, O K edge XANES and TEM. The search for novel Cu-M-O phases has not led to satisfactory results and, at this point, has been discontinued.

EXPECTED STATUS SEP. 30, 2011: The effect of particle size on the thermal behavior of cycled $LiNi_{1/2}Mn_{3/2}O_4$ electrodes will have been evaluated. The effect of different annealing treatments on the structure, composition, and performance of $LiNi_{1/2}Mn_{3/2}O_4$ will have been analyzed. The electrochemical response of NiO during conversion will have been studied at different temperatures. The changes in size and morphology with cycling will have been studied for Sn nanoparticles. Efforts will be directed at making electrodes with these nanoparticles.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; EV: 200 Wh/kg; 1000 cycles.

MILESTONES:
(a) Report the thermal analysis of cycled $LiNi_{1/2}Mn_{3/2}O_4$ electrodes and the results of annealing using different treatments. (Mar. 11) **On schedule**
(b) Report the analysis of Sn nanoparticles at different stages of cycling. (Sep. 11) **On schedule**
(c) Report the electrochemical response of NiO when cycled at high temperatures. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborations: Prof. Grey (SUNY Stony Brook), Drs. Persson, Battaglia, Dong, Doeff, Richardson, Guo (LBNL), Dr. Casas-Cabanas (CRISMAT, France), Dr. Palacin (ICMAB, Spain).

During the first quarter of FY11, work focused on gathering more knowledge of the crystal-chemistry of $LiNi_{1/2}Mn_{3/2}O_4$. This work was done within the *Ni/Mn Focus Group* set up within BATT at the beginning of the fiscal year. The analysis of neutron-diffraction data collected on samples made in air at different temperatures from the same precursors revealed that all of them contained an excess of Mn in the spinel structure, which ranged from 3 to 17% (Table 1). The highest excess was found for the sample prepared at 1000ºC, whereas those prepared at 900°C or below showed minor fluctuations around 5%. The refinement of the data also led to the conclusion that no Li or O vacancies were present in the samples. This Mn excess, together with the Li/O stoichiometry, explained the existence of Mn^{3+} in the materials, as revealed by the electrochemical signature found at around 4.0 V upon cycling in a battery.

The creation of a Mn excess is concomitant to the formation of an impurity with a rocksalt structure. As would be expected, its content increased as the temperature of synthesis (and, hence, the off-stoichiometry) was increased. Transmission electron microscopy (TEM) imaging revealed that the new phase could segregate on the surface of the spinel particles (Fig. 1), thereby changing its chemistry. This phenomenon is likely to affect ion transport and the interaction between electrolyte and electrode at high potentials, one of the critical issues with these materials. While the rocksalt impurity is traditionally proposed to only contain Ni, energy dispersive X-ray spectroscopy (EDS) data indicated that it also contained Mn. The final Mn/Ni ratio was lower than in the original spinel compound, consistent with the creation of Mn excesses as this impurity increased in proportion in the sample.

Sample	Spinel		Rock salt	
	composition	Cell parameter	composition	Cell parameter
OH500	$LiMn_{1.56}Ni_{0.44}O_4$	a=8.1652(1)		
OH600	$LiMn_{1.55}Ni_{0.45}O_4$	a=8.1646(1)		
OH700	$LiMn_{1.53}Ni_{0.47}O_4$	a=8.16439(8) P 4₃ 3 2		
OH800	$LiMn_{1.55}Ni_{0.45}O_4$	a=8.1696(1)	$Li_{0.4}Mn_{0.4}Ni_{0.2}$	a=4.151(2)
OH900	$LiMn_{1.57}Ni_{0.43}O_4$	a=8.2006(8)	$Li_{0.4}Mn_{0.4}Ni_{0.2}$	a=4.142(2)
OH1000 *both phases strongly correlated	$LiMn_{1.67}Ni_{0.33}O_4$	a=8.2866(1)	$Li_{0.4}Mn_{0.36}Ni_{0.24}$	a=4.1473(2)

Table 1. Results of the Rietveld refinement of neutron data for $LiNi_{1/2}Mn_{3/2}O_4$ made at different temperatures.

Figure 1. (bottom) TEM imaging of a particle of "$LiNi_{1/2}Mn_{3/2}O_4$" made at 1000°C, together with EDS results at different points; (top) electron diffraction of the domains in different parts of the crystal.

Work continued toward the other two milestones. Thin films of NiO on Ni were prepared by RF sputtering. These films will be used for electroanalytical experiments at various temperatures, and will become critical above 100°C, where the typical additives in electrodes show spurious reactivity. Work also started on analyzing the electrochemical properties of Sn nanoparticles with sizes ranging from 8 to 15 nm. Results corresponding to these two milestones will be discussed in future reports.
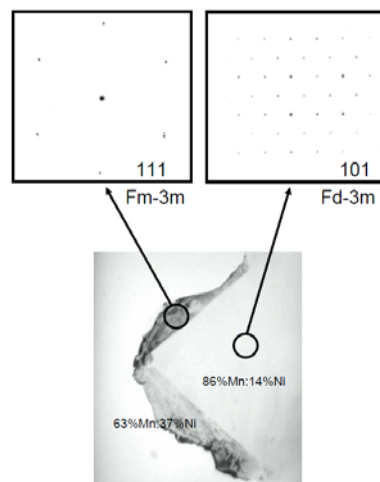
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BATT TASK 5
DIAGNOSTICS

TASK 5.1 - PI, INSTITUTION: Robert Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial Processes: Diagnostics

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Low energy (related to cost), poor Li battery calendar/cycle lifetimes.

OBJECTIVES: (i) Establish direct correlations between electrochemical performance of high-energy Li-ion composite cathodes, and surface chemistry, morphology, topology and interfacial phenomena, (ii) improve the capacity and cycle-life limitations of Li-alloy anodes.

GENERAL APPROACH: Our approach is to (i) apply *in situ* and *ex situ* Raman and FTIR far field and near field spectroscopy/microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, electron microscopy (SEM, HRTEM), and standard electrochemical techniques to detect and characterize bulk and surface processes in intermetallic anodes, and high-energy cathodes, (ii) design and apply a new model electrochemical experimental setup to study the kinetics of lithium alloying and diffusion in intermetallic anodes, and possible correlations with the formation and long-term stability of the SEI layer,

STATUS OCT. 1, 2010: Defined the physico-chemical parameters of the intermetallic alloys and their interfacial properties that determine long-term electrochemical performance of intermetallic anodes in Li-ion systems. These include: (i) charge and mass transfer parameters for Sn, Si, and Al alloys, (ii) basic electrocatalytic properties of alloy materials, (iii) the effect of material structure, crystallinity, morphology and composition. *In situ* and *ex situ* Raman and FTIR spectroscopy were used to determine and characterize surface and bulk processes in composite $LiMnPO_4$ cathodes.

EXPECTED STATUS SEPT. 30, 2011: To gain insight into the mechanism of surface phenomena on thin-film and monocrystal Sn and Si intermetallic anodes and evaluate their impact on the electrode long-term electrochemical behavior. Comprehensive fundamental study of the early stages of SEI layer formation on polycrystalline and single crystal face Sn and Si electrodes will be carried out. *In situ* and *ex situ* far- and near-field FTIR and Raman spectroscopy will be employed in conjunction with AFM surface imaging, which will be applied to detect and monitor surface phenomena at the intermetallic anodes. Similar experimental methodology will be used to detect and characterize surface and bulk processes in high-energy layered NMC and Ni-Mn spinel cathodes.

RELEVANT USABC GOALS: *Cycle life*: 5000 (deep) and 300,000 (shallow) cycles. *Available energy*: 96 Wh/kg. *Calendar life*: 15 years.

MILESTONES:
(a) Identify the structural and surface changes of Si and Sn model anodes working collaboratively with the BATT Anode Group. (Jul. 11) **On schedule**
(b) Carry out preliminary near-filed measurements of SEI layers on Si, Sn anodes and high voltage cathodes. (Sep. 11) **On schedule**
(c) Characterize surface phenomena in high-voltage composite cathodes. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

For the first quarter of FY11, initial work is presented on the diagnostic studies of surface phenomena on the high-voltage cathode material $LiNi_{0.5}Mn_{1.5}O_4$ spinel. An *in situ* electrochemical Raman cell was designed, constructed, and used to observe the surface structural changes of the bare Ni-Mn spinel powder (material synthesized and provided by Jordi Cabana).

A model electrode with the LMNO spinel powder was pressed onto Al foil and assembled into the *in situ* spectro-electrochemical cell. The cell was equipped with Li foil as both counter and reference electrodes and filled with 1M $LiPF_6$ in EC:DEC (1:2 w/w) electrolyte. The CV) of the electrode (Fig. 1) showed two electrochemically active potential regions. The first region at 4.05 V corresponded to the $Mn^{3+/4+}$ redox reaction which originates from a slight excess of Mn in the spinel that resides in the 3+ oxidation state. The two anodic peaks at 4.71 and 4.77 V were attributed to the $Ni^{2+/3+}$ and $Ni^{3+/4+}$ redox reactions, respectively. The CV demonstrates good reversibility of the delithiation/lithiation process, during which Raman spectra of a single aggregated particle were collected.

Figure 1. CV of $LiNi_{0.5}Mn_{1.5}O_4$ powder pressed onto Al foil in the *in situ* Raman electrochemical cell. Raman spectra of one LMNO secondary particle were recorded during the CV at potentials represented by red circles (see Fig. 2)

Before electrochemical cycling, the Raman spectrum of the $Li_xNi_{0.5}Mn_{1.5}O_4$ (x=1) particle in the cell (Fig. 2 "a") was characterized by a superposition of the Ni-Mn spinel Raman peaks at 400, 497, 600, and 636 cm^{-1}, and electrolyte peaks at 360, 524, 715, 730, and 740 cm^{-1}. There were no significant changes in the Raman spectra until the $Ni^{2+/3+/4+}$ redox reactions (spectrum "c"). Three intense new bands at 587, 540, and 482 cm^{-1} that varied in intensity with SOC were attributed to $Ni_{0.5}Mn_{1.5}O_4$. The peak at 587 cm^{-1} was similar to the A_{1g} peak of λ-MnO_2. Therefore this band must have originated from the Mn^{4+}-O stretch whose intensity here was inversely correlated with the Li concentration in $Li_xNi_{0.5}Mn_{1.5}O_4$. All three new bands showed only partial reversibility, suggesting some portions of the aggregate may have lost electrical

Figure 2. (a-g) Baseline subtracted Raman spectra of a $Li_xNi_{0.5}Mn_{1.5}O_4$ particle during CV scan (labels correspond to Fig. 1). Raman spectra of electrolyte and fresh $LiNi_{0.5}Mn_{1.5}O_4$ are shown for reference.

connectivity during the CV measurement. Also noticed upon charging was a large increase in the fluorescent baseline of the spectra, and the weakening intensity of peaks of EC (715 cm^{-1}) and $LiPF_6$ (730 and 740 cm^{-1}). These observations indicated that a layer of electrolyte decomposition products formed on the particle surface due to electrode/electrolyte interactions. In future work toward milestone "c", *ex situ* and *in situ* spectroscopic characterization will be used to investigate the surface and bulk structural changes and electrocatalytic behavior of the Ni-Mn spinel during cycling.

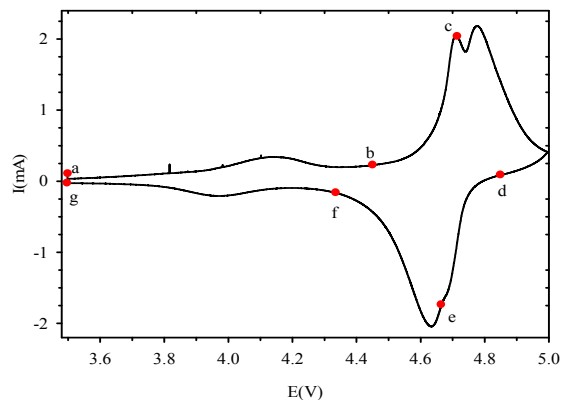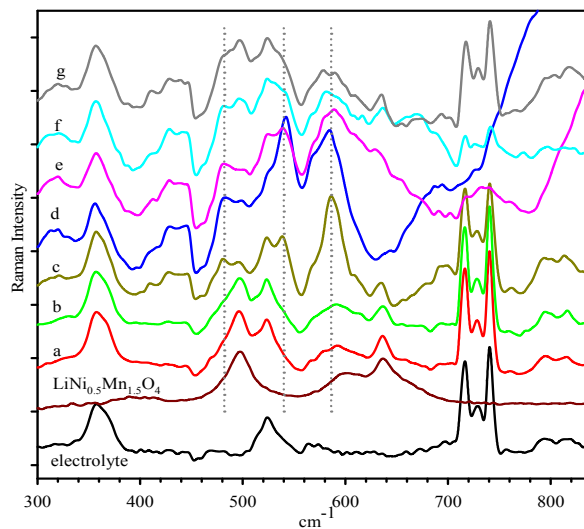Progress toward milestones "b" and "c" is on schedule.

TASK 5.2 - PI, INSTITUTION: Xiao-Qing Yang, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics – Battery Materials: Structure and Characterization

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: PHEV: energy density, cycle life; HEV: power density, abuse tolerance.

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline in helping the development of high energy density lithium battery with better safety characteristics and longer life. The second objective is to design, synthesize and characterize new electrolytes for PHEV oriented high energy density Li/air batteries. Special attention will be given to the new non-aqueous electrolytes with the capability to dissolve Li_2O and Li_2O_2 oxides for Li/air batteries. Testing facilities for high energy Li/air cells and the testing cells using these new non-aqueous electrolytes, as well as gas diffusion electrodes for Li/air cell, will be constructed and investigated at UMASS Boston.

GENERAL APPROACH: Our approach is to use various synchrotron based X-ray techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish the structural differences between surface and bulk of electrodes. Time resolved X-ray diffraction (TRXRD) technique will be used to understand the reactions that occur in charged cathodes at elevated temperatures. *In situ* XRD with PSD detector will be used to monitor the structural changes of the electrode materials during charge-discharge cycling at various C rates. These approaches developed at BNL will be available to other BATT members through extended collaboration. For the task of high energy lithium-air cells, our approach is to combine the organic synthesis and in situ characterization capability with the expertise of air-metal batteries at UMASS Boston to reach the proposed objectives.

STATUS OCT. 1, 2010: We have completed the studies on the structural characteristics of different types of $LiFe_{1-x}M_xPO_4$ (M=Mn, Co, and Ni) phosphate cathode materials using various synchrotron X-ray techniques. The studies of $LiFe_{1-x}Mn_xPO_4$ (x=0.2, 0.4, 0.6, and 0.8) have been completed using *in situ* XRD and XAS spectroscopies.

EXPECTED STATUS SEP. 30, 2011: We will continue our studies on the structural characteristics of different types of lithium iron phosphate cathode materials with mesoporous structure, as well as layer structured $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode materials (in collaboration with ANL) using various synchrotron X-ray techniques. We will continue our Li/air battery studies in non-aqueous electrolytes with gas diffusion electrodes made of carbon materials with various morphologies.

RELEVANT USABC GOALS: 15 year life, <20% capacity fade over a 10-yr. period.

MILESTONES:
(a) Complete soft XAS studies of $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ cathode materials during electrochemical cycling. (Apr. 11) **On schedule**
(b) Complete the studies of carbon structure effects on the electro-catalysis performance of air cathode in Li/air cells. (Apr. 11) **On schedule**
(c) Complete *in situ* x-ray diffraction studies of lithium iron phosphate cathode materials with mesoporous structure in comparison with large particle sized cathode during electrochemical cycling. (Sep. 11) **On schedule**
(d) Complete the studies of increasing the solubility of oxygen in Li-Air electrolytes. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Recent research focused on the Li-rich solid-solution layered cathode materials Li_2MnO_3-$LiMO_2$ (M = Co, Ni, etc.), which exhibit a discharge capacity of more than 200 mAh/g when operated above 4.6 V. However, the mechanism of the charge-discharge reaction, especially for the 4.8V initial charging activation process, has not been clearly understood. There are currently two main mechanisms proposed for the initial charging. The first proposed mechanism suggests that Li^+ extraction is accompanied by oxygen release from the cathode crystals. This is supported by the oxygen gas evolution through *in situ* differential electrochemical mass spectroscopy (DEMS) studies. The second proposed mechanism suggests that Li^+ extraction is not accompanied by oxygen release from the cathode crystals. This mechanism is experimentally supported by the quite small weight change of the cathode during the initial charge beyond 4.5 V. In this mechanism, partially oxidized O_2^- is kept inside the cathode crystals. In collaboration with Dr. Kang and other scientists at ANL, *in situ* and *ex situ* XAS studies by the BNL team at the National Synchrotron Light Source (NSLA) beamlines were carried out to investigate the mechanism of this activation process. Progress was made toward the milestones. The *ex situ* XANES at the Ni K-edge for high energy $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode material before cycling and after the 1st, 2nd, and 3rd charge and discharge are shown in Fig. 1. The Ni K-edge moved to a higher energy position after the 1st charge indicating Ni^{2+} to Ni^{4+} oxidation. On discharge, it moved to a lower energy position than that of the sample before cycling, indicating the full reduction of Ni^{4+}, even lower than the pristine sample. The *ex situ* XANES at the Mn K-edge for the same material before cycling and after the 1st, 2nd, and 3rd charge and discharge are shown in Fig. 2. In contrast to the results shown in Fig. 1, no rigid shift of Mn K-edge was observed, indicating that the Mn ions remain at an oxidation state closer to the Mn^{4+} state.

In collaboration with Prof. Qu and his team at UMASS at Boston, the milestones for Li/air battery are on schedule. The effects of surface modification on preventing carbon surface passivation, which is due to the deposition of Li_2O and Li_2O_2 on to the carbon support, were studied. This investigation revealed that the capacity for the gas-diffusion-electrode (GDE) could be substantially increased if the activated carbon was modified by attaching long-chain hydrophobic molecules to the surface. The carbon surface modification significantly delayed the formation of the dense Li oxide layers, and, thereby, substantially increased the discharge capacity of the GDE.
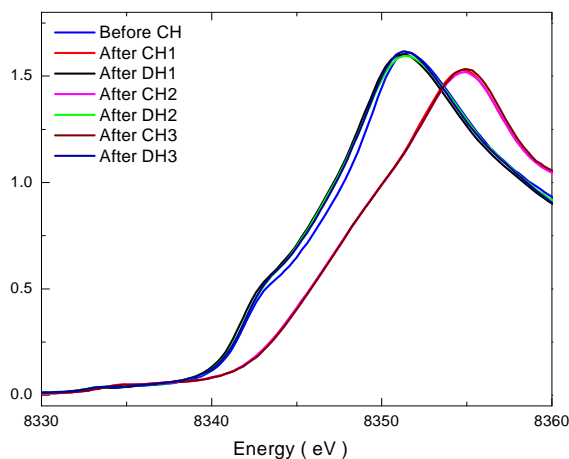

Figure 1. *Ex situ* XAS spectra at Ni K-edge of high energy $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode before cycling and after 1st, 2nd, and 3rd charge and discharge.

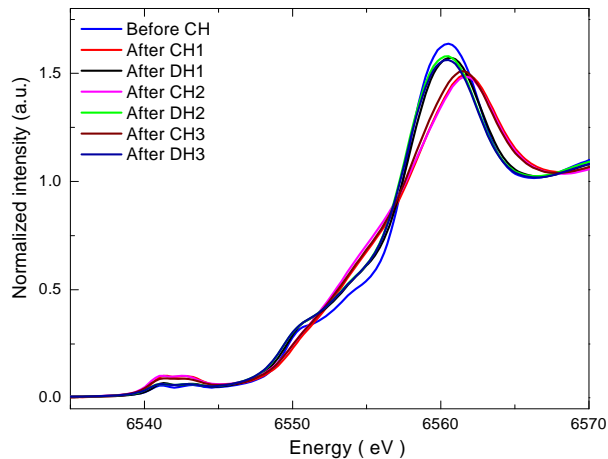**Figure 2.** *Ex situ* XAS spectra at Mn K-edge of high energy $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode before cycling and after 1st, 2nd, and 3rd charge and discharge.

TASK 5.3 - PI, INSTITUTION: Gerbrand Ceder, Massachusetts Institute of Technology, and Clare Grey, SUNY Stony Brook/Cambridge University

TASK TITLE - PROJECT: Diagnostics – First Principles Calculations and NMR Spectroscopy of Electrode Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low rate capabilities; high cost; poor stability; low energy-density

OBJECTIVES: Determine the effect of structure on stability and rate capability of cathodes and anodes. Explore relationship between electrochemistry and particle size and shape. Develop new, stable, cathode materials with high energy-density.

GENERAL APPROACH: Use solid state NMR and diffraction/TEM to characterize local and long-range structure as a function of particle size, sample preparation method, state of charge and number of charge cycles (cathodes). Use electrochemistry to correlate particle size with rate performance. Continue to develop the use of *in situ* NMR methods to identify structural changes and reactivity in oxides and intermetallics and to examine Li dendrite formation. Use first-principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, the effect of structure and particle size on cell voltages and rate capability. Use high-throughput computing to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT 1. 2010: *In situ* NMR and XRD experiments will be ongoing. Several compounds from computational search will continue under experimental investigation.

EXPECTED STATUS SEP. 30, 2011: Go no-go decision will be made on one or two new cathode materials. Initial surface characterizations will be finished. Insights will be gained into the viability of several Na cathodes. Rate performance *vs*. local structure correlations will be established for $Li(Ni_{0.5}Mn_{1.5})O_4$.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:
(a) Initiate Na calculations. (Mar. 11) **On schedule**
(b) Initiate electrochemical testing of one cathode materials in sidorenkite class. (Mar. 11) **On schedule**
(c) Initiate surface characterization. (Mar. 11) **On schedule**
(d) Investigate two new cathode materials and structurally characterize. (Sep. 11) **On schedule**
(e) Explore Li dendrite formation on a series of ionic liquids. (Sep. 11) **On schedule**
(f) Investigate local structure in various $Li(Ni_{0.5}Mn_{1.5})O_4$ spinels and compare with rate performance. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Significant progress was made towards understanding the rate limit in Li-ion batteries with $LiNi_{0.5}Mn_{1.5}O_4$ as the cathode material. In the first stage, the rate at which Li can migrate in the ordered $LiNi_{0.5}Mn_{1.5}O_4$ was investigated by first-principles computation. Figure 1 shows the energy along the migration paths with lowest activation barrier. The corresponding Li diffusivity is about 1.41 to 8.25×10^{-9} cm^2/s. Using the simple estimate $L^2 = Dt$ for the diffusion length, Li can migrate *ca*. 3 μm in 10 seconds. These computational results predicted that $LiNi_{0.5}Mn_{1.5}O_4$ should be able to reach high rate capability even with micron-sized particles.
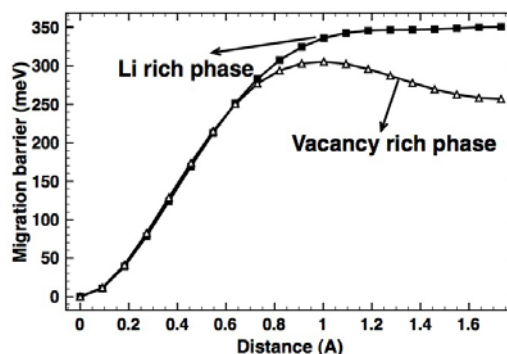

Figure1. Energy barriers along the Li migration path.

To test the rate capability of $LiNi_{0.5}Mn_{1.5}O_4$, phase-pure, ordered material with a particle size between 3 to 5 μm was prepared and assembled in both coin and Swagelok cells. Figure 2 shows excellent discharge capacities. At 0.2C, 147 mAh/g was obtained, which is close to the theoretical capacity of this material. At 20 and 40 C rates, the capacities were still high at 134 and 110 mAh/g, respectively. Excellent cyclability was also achieved. The high rate capability observed is in agreement with the calculated low Li-migration barrier. The $LiNi_{0.5}Mn_{1.5}O_4$ with 3 to 5 μm particle size showed better rate capability than 50 nm $LiNi_{0.5}Mn_{1.5}O_4$.[2] This indicated that ion or electron transport in the particle was not the rate-limiting process, at least at 40 C. Several aspects of the cell configuration were found that could influence the rate performance: 1) comparing Celgard 2500, 2325, C480 separators, C480 gave the best performance;

Figure 2. Discharge rate capability and cyclability of ordered $LiNi_{0.5}Mn_{1.5}O_4$.

2) increasing the pressure on the coin cells led to increased rate performance. This result indicated that contact or wetting issues may have created rate limitations, rather than the material itself.
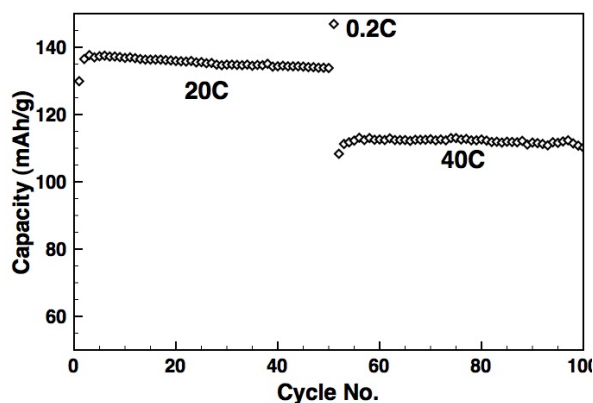
Publications:

(1) X. Ma, B. Kang, G. Ceder, J. Electrochem. Soc., 157(8), A925 (2010).

(2) K. Shaju, P. Bruce, Dalton Trans. 5471-5475 (2008).

Task 5.4 - PI, INSTITUTION: Yang Shao-Horn, Massachusetts Institute of Technology

TASK TITLE - PROJECT: Diagnostics – Studies and Design of Chemically and Structurally Stable Surfaces and Structures of Lithium Storage Materials

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: High cost, poor cycle and calendar life and abuse tolerance of Li-ion batteries

OBJECTIVES: To develop high-energy and long-cycle-life cathodes.

GENERAL APPROACH: The surface-chemistry, microstructure of oxide-electrolyte interface with and without surface modification, and oxide crystal structure will be examined by scanning TEM, synchrotron XRD and XAS, and XPS. These surface and structural features and their changes during electrochemical measurements would provide insights into the nature of interfacial stability between oxide and electrolyte and developing strategies in the design of stable interfaces for high-energy and long-cycle-life cathodes.

STATUS OCT. 1, 2010: The surface-chemistry comparison of pristine and cycled $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ as a function of depth from surface using angle-resolved XPS was completed; from this a working hypothesis on surface species stabilizing the cathode surface was proposed.

EXPECTED STATUS SEP. 30, 2011: Changes in the surface chemistry of select Li-rich $(Li_2O)_x.(MO_2)_y$ (where M = Mn, Co, Ni, etc.) layered compounds will be identified and compared with those of $LiNi_{0.5}Mn_{0.5}O_2$ and $AlPO_4$-coated $LiCoO_2$. Application of fundamental insights to design of new and stable surfaces for high-energy cathodes will be ongoing.

RELEVANT USABC GOALS: High energy/power ratio battery, energy density (>100 Wh/kg, power density (>400 W/kg), 15-year calendar life and cycle life (5,000 cycles).

MILESTONES:
(a) Survey, synthesize, and test select Li-rich $(Li_2O)_x.(MO_2)_y$ (where M = Mn, Co, Ni, etc.) layered compounds. (Mar. 11) **On schedule**
(b) Collect and analyze XPS and TEM data to study the surface-chemistry changes of select Li-rich $(Li_2O)_x.(MO_2)_y$ during charge and discharge. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

The objective of this project is to develop the fundamental understanding necessary to design stable surfaces and structures for Li storage. Our previous research showed three things. 1) An "AlPO$_4$" coating with LiPF$_6$-containing electrolyte can induce fluoride formation in the cycled electrode and reduce the growth of a high-impedance organic layer. 2) Heat-treatment temperature, time, and subsequent annealing can alter the surface chemistry and cation distribution of LiNi$_{0.5}$Mn$_{0.5}$O$_2$, thus, greatly influencing the rate capability at room temperature and high temperatures (such as 40 to 50°C). A large amount of fluoride species also develops on these cycled electrodes, which exhibited stable discharge capacity during cycling even to high voltages. 3) ARXPS can be used to probe the surface chemistry of organic and inorganic components of cycled electrodes as a function of depth from the surface.

Other research: XPS was used to identify the discharge products of oxygen electrochemically reacting with Li ions. The cell consisted of a Li foil, two pieces of Celgard separator (C480), and a cathode of Nafion-bonded Vulcan XC-72 carbon on a separator, supplied by Premetek. The cell was discharged at a constant potential of 2.7 V *vs*. Li in 0.1 M LiClO$_4$ in DME for 10 h and delivered
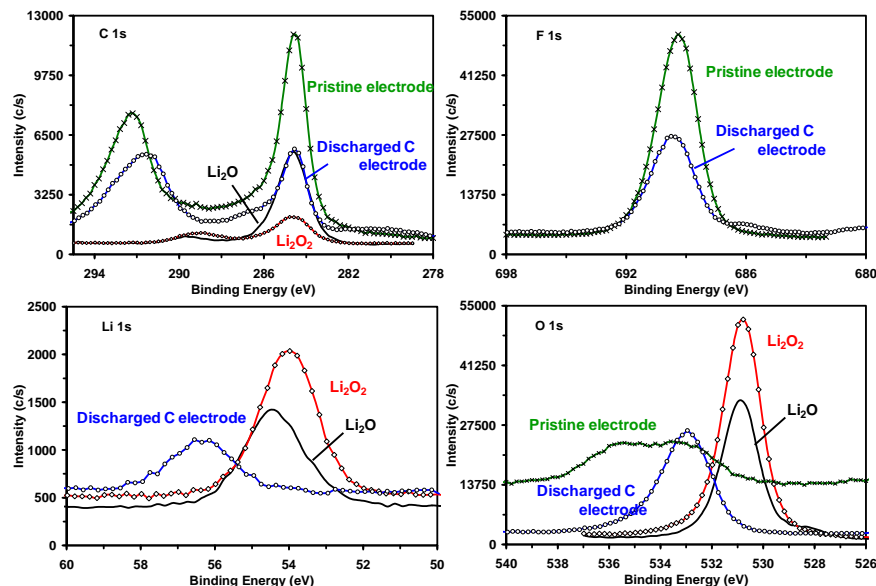

Figure 1: C1s, O1s, F1s and Li1s photoemission lines of pristine and discharged electrode along with Li$_2$O and Li$_2$O$_2$ standards.

a capacity of 1000 mAh per gram of carbon. XPS was conducted using Al Kα X-rays and Li$_2$O and Li$_2$O$_2$ powders as standards. All samples were transferred from an Ar-filled glovebox to the test chamber of the spectrometer without exposure to ambient conditions (Fig. 1). The C 1s region for the pristine and discharged electrode displayed a high binding energy band (291 to 292 eV) due to fluorinated carbon from Nafion, in addition to the hydrocarbon component at 284.6 eV, and some carbon bonding to oxygen with binding energies at 286.2 and 287.5 eV. The F 1s had a binding energy near 689.7 eV and could be attributed to fluorine chemistry in Nafion. The O 1s binding energies for Li$_2$O (530.9 eV) and Li$_2$O$_2$ (530.7 eV) powders were consistent with those reported for LiOH. Based on the O 1s and Li 1s binding energies for Li$_2$O and Li$_2$O$_2$, it was determined that the near-surface regions of these powders consisted of LiOH. The Li$_2$O powder also contained a small fraction (*ca*. 2%) of the O signal with a binding energy of 528.4 eV. This indicated the presence of a small component in the form of Li$_2$O. The O 1s region for the discharged electrode displayed a peak that could be deconvoluted into a major component at 532.9 eV (27.7 at%) and a smaller component at 534.8 eV (4.8 at%). Based on previously reported binding energies for the O1s, the discharge products could be assigned mostly to Li$_2$O$_2$ and possibly a small amount of LiO$_2$.

Collaborations: Collaborations with Dr. A. Mansour, NSWC, continue in XPS and XAS measurements through a subcontract with MIT. Collaborations with M.M. Thackeray, ANL, continue in using TEM to study the atomic structure of Li$_x$Ni$_{0.25}$Mn$_{0.75}$O$_y$ materials.

TASK 6.1 - PI, INSTITUTION: John Newman, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Improved Electrochemical Models

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M LiPF$_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Poor transport properties, capacity, and power fade

OBJECTIVES: Develop experimental methods for measuring transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

GENERAL APPROACH: Use simulations to improve understanding of limitations in cell performance. Develop improved experimental methods for measuring transport and kinetic properties.

STATUS OCT 1, 2010: Experiments comparing the kinetics of different redox shuttles through passivating films on inert surfaces will be ongoing. Modeling the effects of impurities in lithium-ion batteries will be ongoing.

EXPECTED STATUS SEP 30, 2011:   Experiments comparing the kinetics of ferrocene reduction through a passivating film will be complete. Experiments comparing the kinetics of different shuttles through passivating films on inert surfaces will be ongoing. Modeling long-term shape changes in lithium electrodes, including heat and pressure effects, will be ongoing. Modeling the effects of impurities in lithium-ion batteries will be ongoing.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles; 15-year calendar life

MILESTONES:
(a) Develop mechanism for reduction of ferrocene through passivating film. (Oct. 11) C**omplete**
(b) Introduce heat effects into lithium shape-change model. (Jan. 11) **On schedule**
(c) Incorporate stress and strain in ceramics and metals in shape-change model. (May 11) **On schedule**
(d) Initiate rotating disk studies with different redox shuttles. (Aug. 11) **On schedule**
(e) Incorporate stack pressure and anode protection layer in shape-change model. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Modeling Shape Changes in Lithium Electrodes:

Previous work developed a model of the two-dimensional shape change of the Li-metal negative electrode along the in-plane length of the electrode that incorporated kinetics and transport, allowing for the movement of the Li metal. Tabs were included at opposite corners of the positive and negative electrodes causing a non-uniform current distribution (Q3 BATT report). After one full cycle of charge and discharge, a net movement of the Li in the anode was seen where the Li from the center of the electrode shifted toward the negative tab (Fig. 1). Figure 1 shows the dimensionless shape change at 0.5C in the negative electrode after one full cycle to 25% depth of discharge. The dimensionless shape change is calculated by dividing the local value for the amount that the Li moved after a full cycle, relative to its starting position, by the average amount that the Li was depleted after the discharge. Further work will be done to understand the physical phenomena involved in this shape change. Also to be included are the effects of cycle number, depth of discharge per cycle, and pressure and temperature.
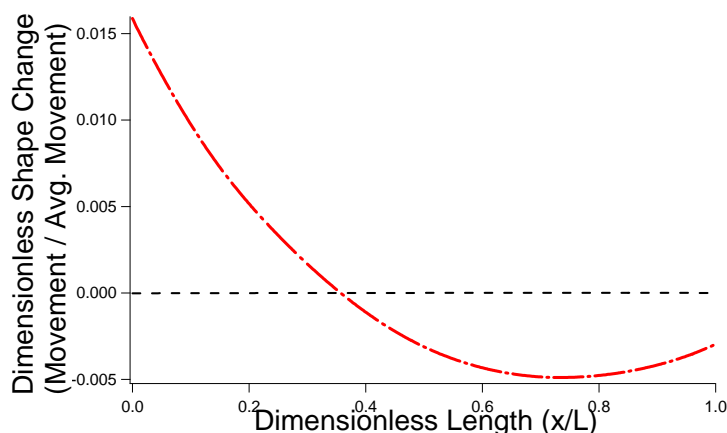

Figure 1. Dimensionless change in the lithium-metal interface after a full cycle (discharge, then charge) at 0.5C and a 25% depth of discharge.

Interaction of Redox Shuttles and the SEI

In the previous report, the steady-state reduction current of ferrocene through a passivating film was described by a simple model of Butler-Volmer kinetics with a through-film limiting current. In this quarter, electrochemical impedance spectros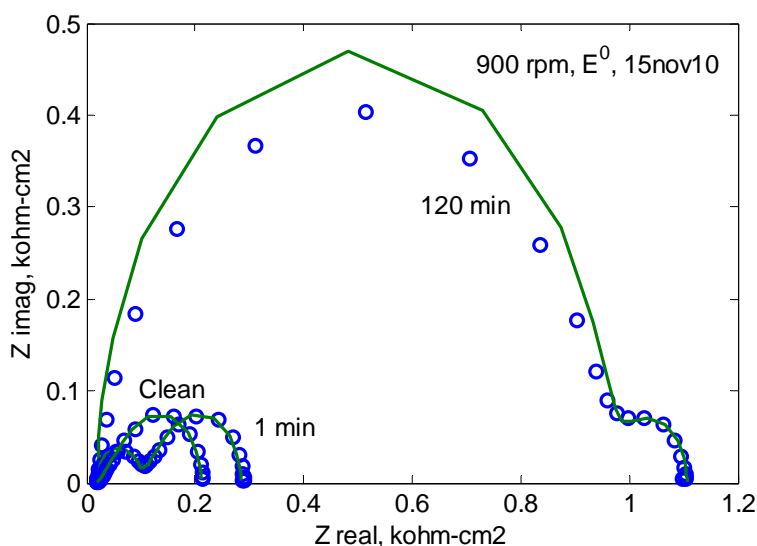copy was used to try to verify the passivation mechanism. Figure 2 shows a Nyquist plot of an electrode passivated at 0.6 V for 0, 1, and 120 minutes. The measurements were all taken at open-circuit conditions and a rotation speed of 900 rpm. Circles show measurements while lines are the model fit. While the real impedance was approximated reasonably well by the model, the imaginary impedance fit was less good. The frequency dependence (not shown) also did not agree perfectly, possibly because of the assumption of a homogenous surface. The current task is to modify the model to account for a distribution of blocked and active sites.

Figure 2. Nyquist plot of electrode passivated for 0, 1, and 120 minutes at 0.6 V. Symbols are measured, line is model fit.

TASK 6.2 - PI, INSTITUTION: Venkat Srinivasan**, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Modeling – Mathematical Modeling of Next-generation Li-ion Chemistries

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: Low energy efficiency; low calendar/cycle life; high cost

OBJECTIVES:
1. Quantify the usefulness of alloy anodes for use in PHEVs.
2. Understand the mechanical degradation in electrodes used in EVs and PHEVs.
3. Model reaction distribution in battery electrodes.

GENERAL APPROACH: Develop mathematical models for candidate Li-ion chemistries. Design experiments to test theoretical predictions and to estimate properties needed for the models. Use models to connect fundamental material properties to performance and degradation modes and provide guidance to material-synthesis and cell-development PIs. Use models to quantify the ability of the candidate chemistry to meet DOE performance goals.

STATUS OCT. 1, 2010: The model development for silicon anode with a NMC cathode was completed. A 1-D model for $LiFePO_4$ that predicts the high rate capacity was completed. A model that accounts for mechanical stress in a single graphite particle was completed.

EXPECTED STATUS SEPT. 30, 2011: The performance models for Si anode with the NMC cathode will be complete and comparison made with the baseline. The degradation of graphite and candidate alloy anodes that takes into account the interaction of the active material and the binder will be complete. A model that accounts for the reaction distribution across the electrode will be developed and compared to experimental data.

RELEVANT USABC GOALS: *Available energy*: 56 Wh/kg (10 mile) and 96 Wh/kg (40 mile); *10-s discharge power*: 750 W/kg (10 mile) and 316 W/kg (40 mile).

MILESTONES:
(a) Compare the performance of the Si/NMC system with the baseline high-energy system and quantify the improvements under PHEV conditions. (Jan. 11) **On schedule**
(b) Extend the mechanical degradation model developed for graphite anode to include volume change and pressure diffusion and report on the possible failure modes. (Mar. 11) **On schedule**
(c) Develop a 2D model for $LiFePO_4$ electrode, and compare the reaction distribution to experimental data. (Aug. 11) **On schedule**
(d) Extend the silicon model to include the effect of mechanical stress and interaction of active material and binder and report on the effect of different binders on degradation. (Sep. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Over the last quarter, significant progress was made toward each of the four milestones. In this report details are presented on the progress in modeling the reaction distribution in porous electrodes and the effect of particle size in predicting electrode behavior in systems with a flat equilibrium potential, such as $LiFePO_4$, $Li_4Ti_5O_{12}$ and $LiMn_{1.5}Ni_{0.5}O_4$. Specifically, it is shown that particle-size effects can lead to path-dependent rate behavior in $LiFePO_4$.

Previously, careful open-circuit relaxation experiments were used to extract the equilibrium potential of the $LiFePO_4$ system, with precise estimation of the width of the single-phase regions where the potential deviates from the flat region. In this quarter, this equilibrium potential was used in a porous-electrode model that incorporated transport in both the solid and electrolyte phases along with two particle sizes, with the goal to understand rate behavior.

During the discharge of the electrode the smaller particles lithiated at a higher rate compared to the larger particles. In systems where the equilibrium potential had a slope, the change in Li content in the small particles resulted in a change in the potential. As the small and large particles were electronically shorted with each other, the lithiation shifted to the larger particles in order to allow the potential of the larger particles to "catch up" to the smaller particles. However, in a flat-potential regime, this self-regulating mechanism did not exist. Therefore, the smaller particle continued to lithiate until the particle reached the single-phase region. In other words, at an intermediate SOC (say 50%), there was a disparity in the level of lithiation between the small and large particles.

Moreover, while on discharge this mismatch led to the small particles having a larger Li content, and on charge, the small particles had a smaller Li content. In other words, there was a path-dependence in the amount of Li in the two particles depending on whether the electrode was charged or discharged. This path dependence had consequences in the rate behavior of the electrode as illustrated in the figure below.

In Fig. 1, the electrode is taken to 50% SOC from either the fully-charged state (black line) or from the fully-discharged state (red line) at a rate of C/25. The electrode was then subject to open-circuit relaxation after which a high rate (5C) discharge was conducted. The figure shows that the electrode starting from the fully-discharged state showed much higher discharge rate capability compared to the electrode that started from the fully-charged state. This unique hysteresis effect explained a phenomenon first reported by our group 6 years ago [V. Srinivasan, and J. Newman, *Electrochem. Solid-State Lett.*, **7**, A30 (2004)]. The model results indicated that the difference in rate capability was more pronounced for electrodes where the particle sizes were very different than that found in a bimodal distribution. The effect described here has broader consequences in understanding the rate behavior of all flat potential systems.
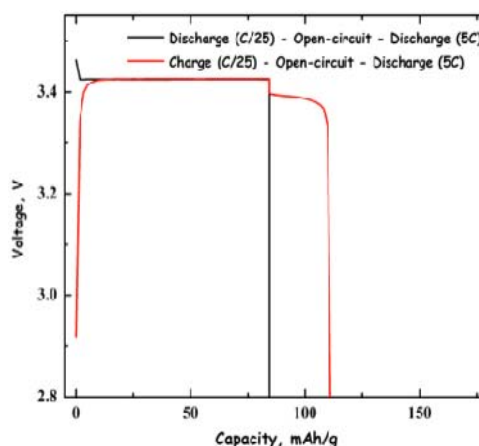

Figure 1. Model results that show a difference in rate capability depending on the previous cycling history. The results provide an explanation for an experimental observation first reported by our group.

TASK 6.3 - PI, INSTITUTION: Ann Marie Sastry, University of Michigan, Ann Arbor

TASK TITLE - PROJECT: Modeling – Thermo-electrochemistry, Capacity Degradation, and Mechanics with SEI Layer

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIER: Prediction of capacity degradation, and excessive conductive mass which penalizes energy and power density and increases cost.

OBJECTIVES: (i) multiscale finite element (FE) modeling considering self-assembly, its effect on cathode structure, and the effect in turn on cathode dissolution as the main effect in capacity degradation, (ii) parametric studies for SEI layer formation, (iii) validation of SEI layer formation model through *ex situ* and/or *in situ* experimental techniques

GENERAL APPROACH: Multiscale modeling of thermal electrochemistry will be extended with microstructure reconstruction *via* self assembly. The precipitation process including a nucleation phase and phase growth is governed by the interfacial energy differences between each species. By evaluating the parameters, we will explore the SEI growth phenomena. The formation and the structure of SEI layers are complex. SEI layers will be characterized and the SEI formation model will be validated by *ex situ* and/or *in situ* experimental techniques.

STATUS OCT. 1, 2010: Modeling of multiscale thermo-electrochemistry has allowed the inclusion of microstructural effects on the performance prediction of Li-ion batteries. SEI layer modeling including nucleation and growth processes has allowed the prediction of the multi-layered structure of SEI layers, which has been confirmed by many experiments. SEI layers formed on $LiMn_2O_4$ composite cathodes were characterized *ex situ* using IR (infrared) spectroscopy and/or Raman, SEM and TEM.

EXPECTED STATUS SEP. 30, 2011: We expect to extend/establish (1) multiscale FE model considering particle aggregation, its effect on cathode structure, and the effect in turn on cathode dissolution as the main effect in capacity degradation, (2) SEI layer formation model and parametric studies for different electrochemical systems, and (3) experimental techniques (using *ex situ* and/or *in situ*) to validate the SEI-layer formation model. Capacity degradation of Li-ion batteries can then be correlated to the properties of SEI layers and particle microstructures.

RELEVANT USABC GOALS: *Available energy for CD mode*: 3.4 kWh (10 miles) and 11.6 kWh (40 miles); *Cycle life*: 5000 cycles (10 miles) and 300,000 cycles (40 miles); *10- s discharge power*: 45 kW (10 miles) and 38 kW (40 miles); *Calendar life*: 15 years (40°C).

MILESTONES
(a) Implement multiscale modeling with self assembly and dissolution. (Mar. 11) **On schedule**
(b) Evaluate parameters such as interfacial energies. (May 11) **On schedule**
(c) Characterize microstructure and chemical elements of SEI layers. (Aug. 11) **On schedule**

PROGRESS TOWARD MILESTONES

The project consists of three separate, but synergistic, research topics focused on a better understanding of the SEI layer: two topics take a computational approach and the third focuses on experimental work to characterize the SEI layer. The following is a summary of research activities on each topic during the quarter (October 1, 2010 to December 31, 2010):

1) **Multiscale modeling with self assembly and dissolution** (Mar. 2011)
Aggregation between additive particles and active particles in the electrode material of batteries strongly affects their interfacial impedance and power performance. Microstructure of percolated particle aggregates was generated using a Brownian dynamics simulation, as shown in Fig.1. (This configuration will also be used in the multi-scale modeling of Li-ion batteries.) The effects of the volume fraction changes due to dissolution in both the active and inert material phases in the composite Li-ion electrodes was investigated by a thermal–electrochemical coupled model. Figure 2 shows the cycling results with different temperature and voltage ranges. Due to a higher temperature and a wider range of voltages, greater dissolution of cathode articles was shown to result in a severe capacity fade.
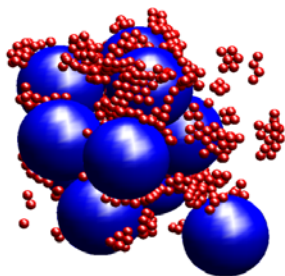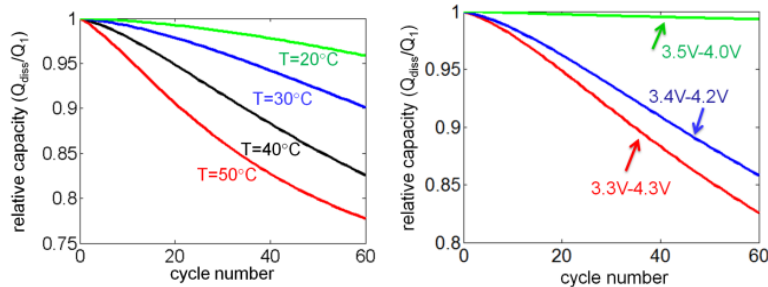

Figure 1   **Figure 2**

2) **Parametric studies for SEI layer formation** (May 2011)
The formation and evolution of the SEI layer were modeled *via* a phase-field model integrating the chemical energy and interfacial energy during the precipitation and growth processes. To explain the origin of the two-layer structure constituting a thin layer and thicker, porous layer, parametric studies using the developed model will be performed by varying the surface and interfacial energies between inorganic species (*e.g.,* LiF, Li_2O) and organic compounds (*e.g.,* ROLi, $ROCO_2Li$).

3) **Characterization of SEI layers** (Aug. 2011)
Cathode samples of the composite $LiMn_2O_4$ system (*i.e.*, $LiMn_2O_4$, PVdF binder, and Carbon Black conductive additive) will be extracted from Swagelok cells after the formation cycling. SEI layers will then be characterized *ex situ*. Characterization results will be used to validate the current SEI-layer formation model. Subsequent cycling will be performed to correlate the SEI-layer properties of Li-ion batteries with the SEI-layer formation model.

TASK 6.4 - PI, INSTITUTION: Kristin Persson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling – Predicting and Understanding New Li-ion Materials Using *Ab Initio* Atomistic Computational Methods

BASELINE SYSTEM: Conoco Philips CPG-8 Graphite/1 M $LiPF_6$+EC:DEC (1:2)/Toda High-energy layered (NMC)

BARRIERS: High cost, low energy, low rate, poor cyclability.

OBJECTIVES: 1) Predict new chemistries and crystal structures for improved electrodes as defined by the goals of USABC. 2) Understand rate-limiting behavior in current electrode materials in order to target and design optimal diffusion properties in new materials.

GENERAL APPROACH: Use computational *ab initio* atomistic modeling methods to understand current Li-ion battery electrode materials and use this knowledge to suggest improvements as well as new electrode materials. Use statistical mechanics models to understand Li diffusion in bulk and on surfaces. Combine and make efficient access to all relevant calculated knowledge in a searchable database, which will greatly facilitate computational materials design.

STATUS OCT. 1, 2010: The analyses of Li diffusion in bulk graphite have been concluded. Evaluation of Al-substitution effect on $LiNi_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO_2$ in terms of Li mobility and electronic conductivity has been studied. Phase diagrams of several Li-Cu-M-O (M= polyanion metal) compounds have been analyzed and the necessary Cu-ion mobility has been bench marked.

EXPECTED STATUS SEP. 30, 2011: Comprehensive studies of surface morphology and Li diffusion on electrode material surfaces (graphite, $Ni_{1/3}Mn_{1/3}Co_{1/3-x}Al_xO_2$ and $LiFePO_4$) will be underway. Investigation of surface band structure of LiFePO4 with/without different surface absorbates will be finished. Conclusion for the Li-Cu-M-O project is expected.

RELEVANT USABC GOALS: PHEV: 96 Wh/kg, 5000 cycles; Operating charging temperature: -30 to 52 ºC

MILESTONES:
(a) Calculate band structure of $LiFePO_4$ surfaces. (Dec. 10) **Delayed, due**
(b) Evaluate $LiCoO_2$ surface electronic structure. (Mar. 11) **On schedule**
(c) Upload materials database. (May 11) **On schedule**
(d) Go/No-go decision on the Cu-Metal-O cathodes. (May 11) **On schedule**
(e) Conclude preliminary evaluation of Li diffusion on $LiCoO_2$ and graphite surfaces. (Jun. 11) **On schedule**

PROGRESS TOWARD MILESTONES

Collaborations: Gerbrand Ceder (MIT), Jordi Cabana, Robert Kostecki, Phil Ross (LBNL).

The electronic structure of $LiFePO_4$ surfaces was investigated in collaboration with Gerd Ceder and Phil Ross. Spectroscopy performed by Dr. Ross on nanoparticle $LiFePO_4$ supplied by MIT showed the nanoparticles to be dark purple, which indicated significantly higher surface electronic conductivity than bulk $LiFePO_4$.

Concurrently, an effort on surface morphology and Li-diffusion modeling to understand transport on the surface of the electrode materials was initiated. As a first step, the Li diffusion on $LiCoO_2$ and on graphitic surfaces as a function of Li chemical potential (the graphite work will be done together with MIT) was studied. The $LiCoO_2$ surface electronic structure has been studied in great detail by XPS and provides a good benchmark for our methods. Also, surface absorbing species on graphite surfaces and anion intercalation, as possible degeneration factors for carbon black, are under investigation.

A postdoctoral researcher was hired in late September 2010 specifically to focus on the surface properties of $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$ and graphite. Unfortunately, the hiring procedure was prolonged because of visa issues, which delayed the start date for these studies. The postdoc will use a combination of atomistic first-principles methods and self-learning potential modeling to investigate surface electronic structure and Li kinetics under different conditions. Figure 1 shows relevant $LiMn_2O_4$ surfaces, which were computed using first-principles methods under the GGA approximation.
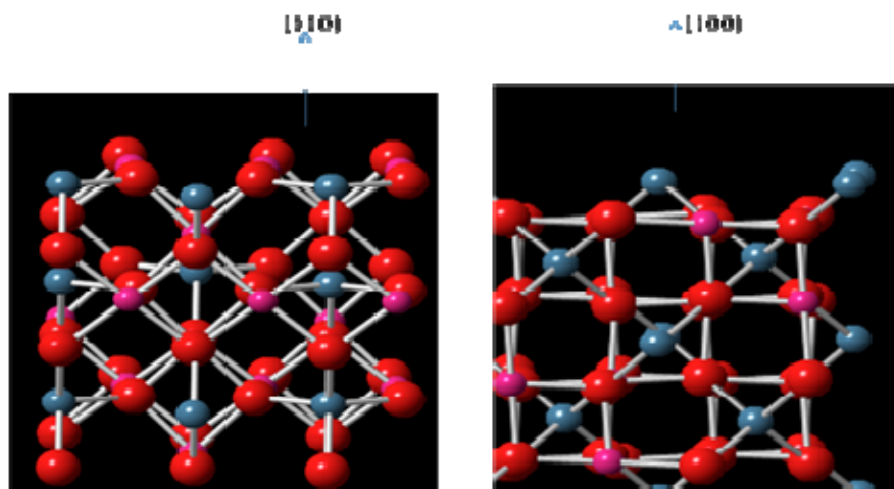

Figure 1. Relevant $LiMn_2O_4$ surfaces.

In order to enable efficient handling of computational data and analyses, a large public database structure is being developed in collaboration with the groups of Gerd Ceder, David Skinner (NERSC), Juan Meza, and David Bailey (CRD LBNL). This searchable database will be able to handle large quantities of data – electronic properties, stability, voltages, etc., and will guide materials design into new-compound territories. The database is being programmed in Python and allows for automatic generation of equation of state, electronic density of states, and band structure for any given symmetry based on original atomic configuration. High-throughput calculations of all known inorganic materials are underway.